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ON THE HYDROLYSIS OF ACID AMIDES.

BY IRA REMSEN.

Investigations[1] carried out many years ago in this laboratory by myself and a number of younger co-workers showed conclusively that generally speaking an oxidizable group like methyl, ethyl, etc., situated in the ortho position relatively to an unoxidizable group or atom (NO_2, Br, SO_3OH, SO_2NH_2) in an aromatic hydrocarbon is protected to a remarkable degree from oxidation when the oxidizing agent is chromic acid, whereas a similar oxidizable group situated in the meta or the para position is easily converted into carboxyl by the same oxidizing agent. This protective influence is shown very clearly in the two following cases: (1, 3, 4)-Metaxylenesulphonamide, $C_6H_3\begin{cases}CH_3 & (1)\\ CH_3 & (3)\\ SO_2NH_2 & (4)\end{cases}$, yields the monobasic acid of the structure $C_6H_3\begin{cases}COOH & (1)\\ CH_3 & (3)\\ SO_2NH_2 & (4)\end{cases}$; and the sulphonamide of the structure $C_6H_3\begin{cases}CH_3 & (1)\\ CH_3 & (4)\\ SO_2NH_2 & (5)\end{cases}$, derived from paraxylene, yields the monobasic acid $C_6H_3\begin{cases}COOH & (1)\\ CH_3 & (4)\\ SO_2NH_2 & (5)\end{cases}$. It is true that

[1] This JOURNAL, **1**, 32, 114; **2**, 50, 130, 405, 413; **3**, 204, 426; **4**, 142, 197; **5**, 106, 149.

to a slight extent the other methyl group in both cases is attacked, but there is no doubt of the fact that it is almost completely protected under the conditions named.

One exception to this rule was observed. When the sulphonamide of mesitylene, $C_6H_2\begin{cases}CH_3 & (1)\\ SO_2NH_2 & (2)\\ CH_3 & (3)\\ CH_3 & (5)\end{cases}$, is treated with chromic acid, it is converted into the monobasic acid of the formula, $C_6H_2\begin{cases}COOH & (1)\\ SO_2NH_2 & (2)\\ CH_3 & (3)\\ CH_3 & (5)\end{cases}$, which appears as the corresponding sulphinide, $C_6H_2\begin{cases}CO\\ SO_2\\ CH\\ CH\end{cases}>NH$.

Later some experiments were made with the object of learning whether reducible groups, more particularly the nitro-group (NO_2), situated in the ortho position to groups or atoms that are not changed by reducing agents, are also protected. Great difficulties were encountered in the course of this work, and the results have not yet been published. These experiments have recently again been taken up but, although some results of value have been obtained, it does not at present appear that it will be profitable to follow this line of work farther.

Much later than the work on oxidation phenomena above referred to came that of Victor Meyer[1] and his students on the esterification of aromatic acids, which shows that when a carboxyl group is situated in the ortho position to two other groups or atoms, as in the dibrombenzoic acid of the formula, $C_6H_3\begin{cases}Br & (1)\\ COOH & (2)\\ Br & (3)\end{cases}$, it is protected from the action of agents which generally have the power to convert acids into their esters. Meyer did not seem to recognize the close connection between his results and those previously obtained in this laboratory; at all events he does not mention them and the most

[1] Beginning Ber. d. chem. Ges., **27**, 510.

favorable view that can be taken of this omission is that he was not familiar with them.

Kellas[1] at the suggestion of Meyer studied the rate of esterification of monosubstituted benzoic acids, and of saponification of the esters of such acids, and in an elaborate article which appeared in 1897 gave an account of the interesting results reached by him. In general, he found that substituted benzoic acids containing the substituting atom or group in the ortho position are converted into their esters much more slowly than the corresponding meta or para acids; and, conversely, that the esters of such ortho acids are saponified much more slowly than the corresponding meta or para compounds.

In 1889 Remsen and Burton[2] found that, while parasulphaminebenzoic acid, $C_6H_4\begin{cases}COOH\\SO_2NH\end{cases}$, is not acted upon when boiled with dilute hydrochloric acid, benzoic sulphinide, $C_6H_4\begin{cases}CO\\SO_2\end{cases}NH$, is first converted into the corresponding ortho acid, $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$, and then into the acid ammonium salt of orthosulphobenzoic acid, $C_6H_4\begin{cases}COOH\\SO_2ONH_4\end{cases}$, by dilute hydrochloric acid. This remarkable difference naturally led to a desire to investigate the action of dilute acids upon acid amides in general—not only those derived from sulphonic acids, but also those derived from carbonic acids. The investigation was, however, delayed for want of a satisfactory method of measuring the rate of change. It was comparatively an easy matter to show that, for example, the amides of benzoic acids containing substituting atoms or groups in the ortho position are more slowly converted into ammonium salts than are the corresponding meta or para acids, but it seemed most desirable to find a refined method by which the exact amount of the change could be determined under a variety of conditions. While we were engaged in testing vari-

[1] Ztschr. phys. Chem., **24**, 221. [2] This JOURNAL, **11**, 403.

ous methods that suggested themselves, and after we had succeeded in devising one that meets all the requirements of the investigation, J. J. Sudborough, P. G. Jackson, and L. L. Lloyd[1] published an account of their investigation of the rate of hydrolysis of the three brombenzamides. They used concentrated sulphuric acid to effect the hydrolysis and reached the conclusion that orthobrombenzamide is "somewhat more stable than the other two." Before the publication of their article the writer had given[2] a brief account of the first results of this investigation. The work has been continued since that time by Dr. Reid, and his account of it follows.

Experiments on the Hydrolysis of Acid Amides.

By E. Emmet Reid.

When an acid amide is heated with a dilute acid it is, as is well known, generally transformed into the corresponding ammonium salt, the elements of water being added as, for example, in the case of benzamide:

$$C_6H_5.CONH_2 + H_2O = C_6H_5.COONH_4.$$

Of course, in the presence of the acid used to effect the change, the ammonium salt represented in the above equation will be converted into free benzoic acid, so that the equation should be written thus:

$$C_6H_5.CONH_2 + AH + H_2O = C_6H_5.COOH + ANH_4.$$

This equation represents the result of complete hydrolysis of the amide. But the reaction requires time, and the time is dependent upon the concentration of the solutions, the temperature, and the nature of the amide. During the course of the reaction, at any time before it is complete, the following equation will represent the substances present, leaving out of consideration the effect of dissociation:

$$xC_6H_5.CONH_2 + AH = aC_6H_5.CONH_2 + bC_6H_5.COOH + bNH_4A + AH.$$

If at any stage of the reaction it were possible to determine how much nitrogen is present as ammonium salt, as distinguished from that which is present in the amide, or, better, if both forms could be determined, we should have it in our

[1] J. Chem. Soc., 1897, 229. [2] This Journal, **19**, 319.

power to follow the course of the reaction. Following a suggestion of Professor H. N. Morse of this laboratory, we have found that by means of freshly precipitated magnesium hydroxide the distinction between the ammonium nitrogen and the nitrogen of the amide, can be made with accuracy. Special experiments have shown that, while the ammonium salts are completely decomposed by boiling them with magnesium hydroxide, the amides are not affected by this reagent. Many of the amides are, however, easily decomposed by caustic alkalies so that the amount of amide remaining in solution in any given case after the ammonium salt has been decomposed can often be accurately determined.

The method of work consists in subjecting weighed quantities of the amides to the action of dilute acids or alkalies of known strength at carefully regulated temperatures and for known periods of time. At regular intervals of time measured quantities of the solutions are removed, and the two forms of nitrogen, or of ammonia, determined by the method above referred to.

Calculation of Results.

If A represents the original concentration of acid or alkali used, and B that of the amide, then after a time, t, these will have become $A-x$ and $B-x$. If the reaction proceeds regularly the velocity at any time should depend on the product of the concentrations at the time.

Then

$$v = \frac{dx}{dt} = (A-x)(B-x)K,$$

in which K is a constant depending on the nature of the reacting substances, and on the temperature.

On integrating $$\frac{dx}{(A-x)(B-x)} = Kdt;$$

it becomes $$\frac{1}{A-B} \log. \frac{A-x}{B-x} = Kt + C.$$

Making $x = 0$, we have

$$\frac{1}{A-B} \log. \frac{A}{B} = C.$$

Substituting this value for C in the above we get

$$\frac{1}{A-B}\log.\frac{A-x}{B-x}=Kt+\frac{1}{A-B}\log.\frac{A}{B}.$$

Transforming

$$K=\frac{1}{(A-B)t}\log.\left\{\frac{A-x}{B-x}\cdot\frac{B}{A}\right\}.$$

If ordinary logarithms are used this must be multiplied by 2.3025.

Then

$$K=\frac{2.3025}{(A-B)t}\cdot\log.\left\{\frac{(A-x)}{(B-x)}\cdot\frac{B}{A}\right\}.$$

This equation has been used by a number of chemists. Since $C_\infty=A-B$, $C_t=A-x$, while $C_1-C_\infty=A-(A-B)=B$, $C_1=A$, and $C_t-C_\infty=A-x-(A-B)=B-x$, it is the same as van't Hoff's expression

$$K=\frac{2.3025}{C_\infty t}\cdot\log.\frac{Ct(C_1-C_\infty)}{C_1(C_t-C_\infty)}.$$

The equation

$$Kt=\frac{1}{A-B}\cdot\log.\frac{(A-x)}{(B-x)}\frac{B}{A}$$

may be written $\log.\frac{(A-x)}{(B-x)}\frac{B}{A}=(A-B)Kt$, or

$$\frac{B}{A}\cdot\frac{A-x}{B-x}=e^{(A-B)Kt}=[e^{(A-B)K}]^t=m^t.$$

Many chemists in testing the equation

$$\frac{dx}{dt}=(A-x)(B-x)K$$

have for the sake of simplicity put $A=B$. In case the reaction is slow this would necessitate making A and B very large which might be impossible on account of the slight solubility of one of the substances; or, for some other reason, it might be undesirable. By making A and B very small when K is very small, the velocity might be so slight that the exper-

iments would take long periods of time. There is a worse difficulty for, if $A—B = C$

then $$\frac{dx}{dt} = (A—x)(B—x)K$$

becomes $$\frac{dx}{dt} = C(B—x)K + (B—x)^2K.$$

Even when C is large, towards the end of the reaction the velocity gets very small and difficult to measure; but, if $C = 0$ the velocity sooner reaches a limit where it cannot be measured. Fair results were obtained with $A = 28B$. When $\frac{24}{25}B$ had been used up, the velocity had about $\frac{27}{28} \times \frac{1}{25} = \frac{1}{28}$ (nearly) its original value while with $A = B$ after 96 per cent had been decomposed the velocity would have been only $\frac{1}{25} + \frac{1}{25} = \frac{1}{625}$, its orginal value.

In the experiments described in this article, B was always made 100 in calculating the value of $\log. \frac{A—x}{B—x}$; since x was most readily calculated in percentages, A was expressed in corresponding units. This, of course, does not change the value of the fraction.

In all the tables given in this article

$$K = \frac{2.3025}{(A—B)t} \cdot \log. \left\{ \frac{(A—x)}{(B—x)} \cdot \frac{B}{A} \right\}.$$

PREPARATION OF MATERIAL.

For the experiments in Groups I and II, commercial ortho-, meta- and paranitrobenzoic acids were recrystallized until they were pure, and then converted into the corresponding amides. For the other experiments, *o*-nitrobenzoic acid was prepared partly from benzoic acid and partly by oxidizing *o*-nitrotoluene with potassium permanganate. *m*-Nitrobenzoic acid[1] was made by nitrating benzoic acid. *p*-Nitrobenzoic acid was obtained by oxidizing *p*-nitrotoluene. For this purpose it was found best to add 200 grams of *p*-nitrotoluene to 1100 grams concentrated sulphuric acid, 1200 cc. water and 750 grams sodium bichromate, in a five-liter flask provided with a condenser

[1] It was found that even much colored solutions of *m*-nitrobenzoic acid can be decolorized, and made to yield very white acid by adding, while hot, a little potassium permanganate and a few drops of sulphuric acid.

tube. The mixture is kept gently boiling for forty or fifty hours. The residue of *p*-nitrotoluene may be recovered by distilling with steam, but it is not worth the trouble. The *p*-nitrobenzoic acid is filtered off, and well washed. It is then dissolved in soda and this solution treated with charcoal. The acid is precipitated with hydrochloric acid and is pure enough for most uses. From 600 grams *p*-nitrotoluene treated as above 45 grams were recovered and 547 grams of *p*-nitrobenzoic acid obtained. Sodium bichromate is far preferable to the potassium salt.

o-Chlorbenzoic acid[1] was made by oxidizing *o*-chlortoluene with potassium permanganate. Some of the *o*-chlortoluene was purchased, and some made by the diazo reaction from *o*-toluidine.[2]

p-Chlorbenzoic acid was made by oxidizing commercial *p*-chlortoluene with chromic acid mixture which burnt up the most of it.

m-Brombenzoic acid[3] was made by heating benzoic acid, bromine and water in sealed tubes. An attempt was made to free it from benzoic acid by passing steam through a flask containing it.[4] It was finally purified by heating to 200°C. with fuming sulphuric acid and afterwards heating alone in a retort to 280° C.[5] After recrystallizing from hot water it was pure.

p-Brombenzoic acid[6] was obtained by oxidizing *p*-bromtoluene with chromic acid mixture. Crude bromtoluene was used. This acid is easily obtained in any quantity.

o-Iodobenzoic acid[7] was prepared by oxidizing *o*-iodotoluene with nitric acid diluted with twice its bulk of water. Several weeks' boiling is required, and the yield is poor. The acid was filtered off occasionally and the unchanged *o*-iodotoluene returned, with the nitric acid, to the flask for further heating.

m-Iodobenzoic acid[8] was obtained by diazotizing *m*-amido-

[1] Richter: Ber. d. chem. Ges., **4**, 463; Emmerling: *Ibid.*, **8**, 880.
[2] Graebe: Ann. Chem. (Liebig), **276**, 56.
[3] Hübner: *Ibid.* **143**, 233.
[4] Angerstein: *Ibid.*, **158**, 5.
[5] Hübner: *Ibid.*, **149**, 131.
[6] Jackson and Rolfe: This JOURNAL, **9**, 84.
[7] Kekulé: Ber. d. chem. Ges., **7**, 1007.
[8] *m*-Amidobenzoic acid was diazotized according to the directions given for *o*-amidobenzoic acid by Wachter, Ber. d. chem. Ges., **26**, 1744.

benzoic acid, which, in turn, had been made by reducing *m*-nitrobenzoic acid. The *m*-iodobenzoic acid was purified by sublimation.

p-Iodobenzoic acid[1] was made by oxidizing *p*-iodotoluene, either with potassium permanganate or nitric acid. The latter seemed preferable though it acts slowly. The *o*- and *p*-iodotoluenes were made according to Gattermann's directions for making iodobenzene, using equivalent quantities of *o*- and *p*-toluidines. The yield of the para is good.

o-, *m*-, and *p*-Toluic acids were purchased.

o-Methoxybenzoic acid was made by oxidizing with potassium permanganate the methyl ether of *o*-cresol, which was made according to Alleman's directions for making the methyl ether of *p*-cresol.[2]

Preparation of the Amides.—All of the above acids were converted into their amides as described below. The yields were in some cases nearly quantitative, in others not so good, but always fair.

The acid was dried and powdered and put into a strong flask, slightly more than the calculated amount of powdered phosphorus pentachloride added, and the flask vigorously shaken. Sometimes slight warming was necessary to start the reaction. When the reaction was nearly over the flask was exhausted as nearly as possible by connecting with a filter-pump. The flask was meanwhile placed in a vessel of water which was brought to boiling and kept there for some time. When the phosphorus oxychloride was about all driven off, the acid chloride was cooled and dissolved in several volumes of ether. This solution was allowed to run with vigorous stirring, into a mixture of crushed ice and concentrated ammonia water.

The amides thus made were recrystallized from hot water, usually twice, and found to be pure.

o-, *m*-, and *p*-Amidobenzamides were made by heating for several days solutions of the corresponding nitrobenzamides, with ammonium sulphide. The meta-amide is very soluble. It was recrystallized three times.

o-Hydroxybenzamide was made by heating oil of winter-

[1] Beran: *Ibid.*, **18**, 137; Hofmann: Ann. Chem. (Liebig), **264**, 160; Gattermann: Praxis, p. 187.

[2] Dissertation, Johns Hopkins University, 1897, p. 8.

green in sealed tubes with concentrated ammonia water. The yield is good. The amide is very soluble.

p-Hydroxybenzamide was made by heating ethyl paroxybenzoate in sealed tubes with concentrated ammonia water. Some phenol is formed and the yield of the amide is poor.

o-Ethoxybenzamide was made by heating methyl ethylsalicylate with concentrated ammonia water in a sealed tube at 130° C. The methyl ethylsalicylate was prepared by heating in a sealed tube oil of wintergreen, ethyl iodide, and caustic potash in equivalent quantities.

The amides studied seem, in general, to be considerably more soluble than the corresponding acids. The order of solubility is about that of the acids.

p-Chlor- and *p*-nitrobenzamides are difficultly soluble, while the *p*-brom-, and *p*-iodobenzamides are very slightly soluble even in hot water.

The melting-points of these amides were taken with a thermometer said by Bender and Hobein to read 0.7° too low at 0° C., 0.5° too low at 100° C., and correct at 200° C. They were as follows :

Amide.	M. p. observed.	Cor.	Given in literature.
o-Nitro-	172–172.2	176.6	173, 174, 176
m-Nitro-	140–140.2	142.7	140, 142
p-Nitro-	196	201.4	198
o-Chlor-	139.9	142.4	139
p-Chlor-	174–174.2	178.3	170
m-Brom-	152.3	155.3	150
p-Brom-	185.2	189.5	186–190
o-Iodo-	179.4	183.6	183
m-Iodo-	182–182.2[1]	186.5	....
p-Iodo-	210.6–210.8	217.6	....
o-Hydroxy-	137.4	139.9	138
m-Hydroxy-	167	170.5	167
p-Hydroxy-	....	....	162
o-Amido-	....	....	108
m-Amido-	....	....	75, 78, 79
p-Amido-	178.3–178.6	182.9	178–179
o-Methoxy-	126.5	129.0	128–129
p-Methoxy-	....	....	162–163
o-Ethoxy-	130	132.1	132–135
o-Toluic	139.8	142.8	138
m-Toluic	93	94.0	....
p-Toluic	157.5	160.8	151–159

[1] Sublimed 180°.

The following amides were successfully analyzed for nitrogen by dissolving in 200 cc. water, adding 10 grams caustic soda and distilling off the ammonia into acid, which was 0.1433 normal.

Amide.	Weight.	No. cc. of acid.	N_3.	Found N per cent.	Calculated N per cent.
m-Nitro-[1]	250 mg.	10.48 cc.	= 21.03 mg.	8.42	8.49
"	" "	10.51 "	= 21.06 "	8.44	8.49
p-Nitro-[1]	250 "	10.50 "	= 21.07 "	8.44	8.49
"	" "	10.63 "	= 21.33 "	8.55	8.49
m-Amido-	232 "	10.62 "	= 21.31 "	9.19	9.15
m-Brom-	226 "	7.89 "	= 15.79 "	6.99	7.05
p-Brom-	301 "	10.47 "	= 21.00 "	6.97	7.05
o-Chlor-	234 "	10.70 "	= 21.47 "	9.18	9.07
p-Chlor-	234 "	10.60 "	= 21.27 "	9.10	9.07
m-Toluic	203 "	10.47 "	= 21.00 "	10.35	10.44
p-Toluic	203 "	10.51 "	= 21.08 "	10.39	10.44

EXPERIMENTS.—GROUP I.

Hydrolysis of o-, m- and p-Nitrobenzamides with Hydrochloric and with Sulphuric Acids.

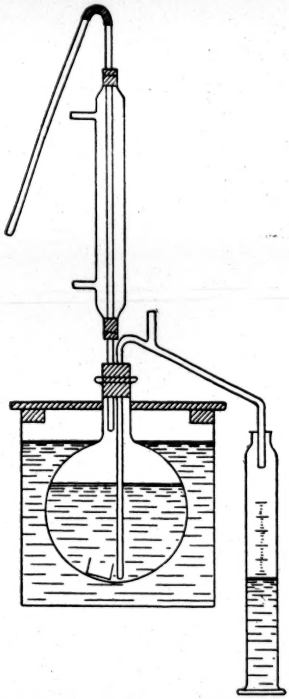
Apparatus for Heating Amides, and Method of Taking Samples.

600 cc. of the acid of the desired strength were placed in a 1-litre balloon flask, which was suspended in a covered water-bath containing about 8 litres of water, which was kept vigorously boiling. It was generally kept full by a constant level attachment. Sometimes the water which was run in was heated previously. The water-bath was surrounded by asbestos and the cover was furnished with the same. The flask was provided with a rubber stopper carrying 2 tubes like a wash-bottle except that the one which reached only through the stopper was straight and its upper part surrounded by a Liebig condenser jacket some 30 cm. in length, while the exit tube extended out beyond the edge of the bath and was provided with a T blown on just beyond its highest point.

When it was certain that the acid in the flask had reached the temperature of the bath the stopper was momentarily removed and the amide, which had been weighed out in a light open-mouthed capsule, was dropped in and the flask shaken for one or two minutes so as to insure the complete solution

[1] That is,—in the amide group.

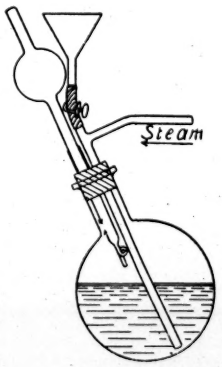
of the amide. The time was kept by a watch which was always set at a chosen hour exactly, so that the samples always fell due when the hands were in the same positions. This makes the timing much easier and prevents many errors.



Two flasks were always heated in the same bath. In the one *m*-nitrobenzamide was put, and into the other *p*-nitrobenzamide. The one was put in just five minutes before the other, and exactly the same interval was allowed in taking out the samples.

At the proper time the desired amount of liquid was forced out by blowing into the upright tube, the branch of the exit tube being closed until the moment the liquid ceased flowing, when it was opened so as to allow that portion in the outer part of the tube to flow out. The amount taken out each time was as near as convenient to 75 cc. The sample was received in a 250-cc. cylinder containing 150 cc. cold water. In this way the temperature is immediately reduced to about 45° C. at which the reaction would, at best, go on extremely slowly, and the acid is diluted to about one-third of its former strength. The operation of taking a sample required about three seconds. After the taking of each sample the outer part of the exit-tube was washed out by pouring a little alcohol down the branch tube. The samples were poured into flasks, the cylinder being washed out twice each time. These flasks were set aside in regular order, and analyzed in the order in which they were taken out.

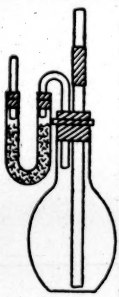
Analysis of Samples.—The sample to be analyzed was poured into a balloon containing about 750 cc. and washed out twice, the washings being added to the sample. 10 cc. of a solution containing 0.5 gram of magnesium sulphate to the cubic centimeter was added, and then caustic soda solutions in small portions until a slight precipitate of magnesium hydroxide remained after shaking, and finally 2 to 2.5 cc. of a solution of the same containing 0.26 gram sodium hydroxide per cc., which was known to be enough to precipitate about two-thirds of the magnesium as hydroxide.



The flask was connected by means of a bulb-tube with a block-tin condenser, and the ammonia distilled off in the usual manner. Steam was passed into it meanwhile to expedite the carrying over of all the ammonia. The tube which carried in the steam had a branch at its highest point which was

closed but which was opened when the steam was cut off, to prevent "sucking back." The steam was supplied from a flask containing a little sulphuric acid and potassium bichromate.

The distillate was caught in a 500-cc. Florence flask containing a little more standard acid than was judged sufficient for the ammonia expected in each case. This flask was closed by a rubber stopper carrying a large tube which extended to the bottom, and at its upper end it was connected to the end of the condenser by a piece of rubber tubing. A smaller tube served to connect the receiver with a U-tube of soda-lime to protect it from the carbon dioxide of the air. When it was thought that sufficient distillate had been collected, the receiver was removed and replaced by a beaker containing litmus. This often showed no trace of ammonia and in most others only minute traces. In some cases an appreciable amount was found, and this was neutralized by a fraction of a drop of standard acid, which was added to the amount put in the receiver, and the distillation continued until no appreciable amount of ammonia came over.



The burner was turned out and the steam cut off and another receiver containing standard acid was connected with the condenser, and 20 cc. of a solution containing 0.5 gram of sodium hydroxide per cc. was run into the balloon by means of a funnel connected with the branch of the steam tube.

The strong caustic soda solution hydrolyzes the *m*- and *p*-nitrobenzamides in a very short time. In fact, using the above amount it is just as easy to determine the ammonia from these amides as from ammonium chloride. The contents of each receiver were emptied into a beaker, the receiver being washed out with water which had been distilled from acid and then from alkaline potassium permanganate, and kept in a special wash-bottle well protected from the carbon dioxide of the air. The excess of acid was titrated back with standard ammonia, litmus being used as indicator. The method of titration was always the same. The standard am-

monia was allowed to drop in from a burette, stirring meanwhile, until a blue color appeared, a few drops of acid was added, and the ammonia added, a drop at a time, until a blue color appeared, the readings were taken and a few drops of acid added, and then titrated to blue color again, and the readings taken. The results given by these two titrations were averaged each time. A number of test analyses were made by this method which gave satisfactory results.

Each of the amides in question was boiled for hours with the magnesia mixture and no appreciable amount of ammonia could be found in the distillates.

The results were calculated by adding the number of cubic centimeters of standard acid neutralized by the ammonia in the two stages and dividing this into the number neutralized by the first. Hence the strength of the standard acid used was unimportant, yet it was standardized with care.

In the experiments up to Series III cochineal was used as an indicator, and the above precautions to guard against carbon dioxide were not taken, but otherwise the method of analysis was the same.

It was not found practicable to determine *o*-nitrobenzamide as above; hence, in the few experiments made with it, a sample was taken in each of a number of small dry flasks and a measured amount of the solution taken from each; the flasks had been cooled quickly by holding them in a stream of cold water. The amount of decomposition was found by ascertaining the amount of ammonium chloride present by distilling as above with the magnesium hydroxide. In this case the number of cubic centimeters of standard acid neutralized was divided by the number equivalent to the amount of *o*-nitrobenzamide known to have been present in the amount of the solution taken.

In the following tables x = per cent of decomposition or hydrolysis found.

t = time, always stated in minutes.

A = conc. of acid.

B = conc. of amide, always = 0.04026 N.

Series I.

o-Nitrobenzamide with Hydrochloric Acid.

$A = 0.4149$ N. $B = 0.04026$ N. Titrations with H_2SO_4, 0.1419 N.

4.000 grams put in flask with 600 cc. hydrochloric acid.

No. cc. in sample.	No. cc. of stand. acid neutralized.	Equiv. of total amide in sample in cc. stand. acid.	Per cent. hydrolyzed.	Time in minutes.
96.6	0.95	27.41	3.5	180
91.2	1.03	25.86	4.0	240
82.5	1.33	23.40	6.0	360
86.0	2.16	24.40	8.8	480

The samples taken for times less than three hours were not analyzed as they were then not thought to contain enough ammonia. Corresponding experiments were made with the meta- and para-amides, but the analyses were not all satisfactory, as not enough liquid was caught in the distillations to make sure of the ammonia.

Series II.

m- and p-Nitrobenzamides.

Conc. HCl $= A = 0.4896$ N. Conc. amide $= B = 0.04026$ N. Temp. 100° C. Standard $H_2SO_4 = 0.1419$ N.

The number of cubic centimeters of standard acid neutralized in the first distillation is given in column 1 and represents the amide hydrolyzed; that neutralized in the second distillation, with caustic soda, represents that not hydrolyzed, or the unchanged part.

Metanitrobenzamide.

t.	Changed.	Unchanged.	Total.	Per cent. hydrolyzed.
30	5.35	19.95	25.30	21.1
60	8.70	11.59	20.29	42.8
90	9.69	9.65	19.34	50.1
120	11.39	6.14	17.53	65.0
180	15.12	3.66	18.78	80.5
240	17.88	2.24	20.12	88.9
300	19.69	1.58	21.27	92.6
360	18.81	1.17	19.98	94.2

Paranitrobenzamide.

t.	Changed.	Unchanged.	Total.	Per cent. hydrolyzed.
30	5.29	16.41	21.70	24.4
60	8.49	9.11	17.60	48.2
90	12.52	7.22	19.74	63.4
120	13.69	5.55	19.24	71.2
180	16.25	2.97	19.22	84.5
240	19.90	1.75	21.65	91.9
300	24.51	1.41	25.92	94.6
360	19.34	0.63	19.97	96.9

The results for thirty minutes are low, as time is required for solution.

Series III.

Conc. hydrochloric acid $= A = 0.9792$. $B = 0.04026$. $A-B = 0.9389$. $A/B = 24.35$. Stand. H_2SO_4, 0.1419 N.

Metanitrobenzamide.

	t.	Changed.	Unchanged.	Total.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	10.79	14.84	25.63	42.1	2393	57.9	0.0188
Jan. 27, 1897	60	10.40	4.67	15.07	69.0	2366	31.0	0.0203
	90	17.19	3.67	20.86	82.4	2353	17.6	0.0202
Temp. 100.1° C.	120	10.10	1.67	11.77	85.8	2349	14.2	0.0170
	150	17.00	1.12	18.12	94.9	2340	5.1	0.0208
	180	18.04	0.62	18.66	96.7	2338	3.3	0.0199
Average constant = 0.0194	210	19.32	0.46	19.78	97.7	2337	2.5	0.0189
	240	31.97	0.38	32.35	98.8	2336	1.2	0.0195

Paranitrobenzamide.

	30	10.12	10.29	20.41	49.6	2385	50.4	0.0236
Feb. 1, 1897	60	15.88	4.90	20.78	76.4	2356	23.6	0.0251
	90	17.57	4.37	19.94	78.1	2347	11.9	0.0249
Temp. 100.2° C.	120	20.69	1.28	21.97	94.2	2341	5.8	0.0255
	150	16.29	0.68	16.97	96.0	2339	4.0	0.0230
	180	20.25	0.30	20.55	98.5	2337	1.5	0.0246
Average constant = 0.0237	210	21.09	0.28	21.37	98.7	2336	1.3	0.0218
	240	46.63	0.45	26.88	99.2	2336	0.8	0.0212

Series IV.

HCl conc. = A = 0.2448 N. B = 0.04026. $A-B$ = 0.2045. A/B = 6.080. Standard H_2SO_4 = 0.1419 N. Feb. 15, 1897.

Metanitrobenzamide.

	t.	Changed.	Unchanged.	Total.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
Temp. 100° C.	60	4.51	16.33	20.84	21.6	586	78.4	0.0167
	120	9.20	12.57	21.77	42.3	566	57.7	0.0195
	180	11.44	9.06[1]	21.10	54.2	554	45.8	0.0187
	240	10.94	6.05	16.99	64.4	544	35.6	0.0188
	300	14.42	5.50	19.92	72.4	536	27.6	0.0189
	360	15.24	4.19	19.43	78.5	530	21.5	0.0190
Average constant = 0.0186	420	16.87	3.76	20.63	81.8	526	18.2	0.0181
	480	23.90	3.88	27.78	86.4	522	13.6	0.0188

Paranitrobenzamide.

	60	5.78	13.77	19.55	29.5	579	70.5	(0.0246)
	120	10.49	12.28	22.77	46.2	562	53.8	(0.0221)
	180	14.60	8.31	23.91	65.2	543	34.8	(0.0256)
	240	14.84	6.17	21.01	70.6	537	29.4	0.0224
	300	15.35	4.35	19.70	77.9	530	22.1	0.0224
	360	14.21	2.81	17.02	83.5	525	16.5	0.0225
Average constant = 0.0223 or 0.0228	420	15.91	2.41	18.32	86.8	521	13.2	0.0220
	480	16.39	1.73	18.12	90.5	518	9.5	0.0223

[1] There is an error here, the cause of which I cannot determine.

Series V.

$H_2SO_4 = A = 1.128$ N. $B = 0.04026$. $A-B = 1.088$. $A/B = 28.02$ Standard $H_2SO_4 = 0.1419$ N. Feb. 23, 1897.

Metanitrobenzamide.

	t.	Changed.	Unchanged.	Total.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
Temp. 100° C.	30	6.10	13.82	19.92	30.6	2772	69.4	0.01086
	60	9.30	10.28	19.58	46.8	2755	53.2	0.00942
	90	14.48	8.93	23.41	61.9	2740	38.1	0.00963
	120	13.58	4.88	18.38	73.4	2729	26.6	0.00990
	150	15.90	3.94	19.84	80.1	2722	19.9	0.00971
	180	15.05	2.97	18.02	83.5	2719	16.5	0.00904
Average constant = 0.0097	240	17.29	1.56	18.85	91.9	2710	8.1	0.00946
	300	29.21	1.31	30.52	95.8	2706	4.2	0.00961

Paranitrobenzamide.

	30	4.45	11.91	16.36	26.9	2775	73.1	0.0093
	60	11.53	10.60	22.13	52.1	2750	47.9	0.0110
	90	11.76	6.03	17.79	66.5	2736	33.5	0.0109
	120	14.79	5.13	19.92	74.9	2727	25.1	0.0104
	150	18.65	3.86	22.51	82.9	2719	17.1	0.0106
	180	19.55	2.81	22.36	87.6	2714	12.4	0.0105
Average constant = 0.0104	240	9.85	0.82	10.67	93.3	2709	6.7	0.0102
	300	22.80	0.88	23.68	96.4	2706	3.6	0.0101

Series VI.

$H_2SO_4 = A = 0.564$ N. $B = 0.04026$ N. $A-B = 0.524$. $A/B = 14.01$. Standard $H_2SO_4 = 0.1419$ N. March 1, 1897.

Metanitrobenzamide.

	t.	Changed.	Unchanged.	Total.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
Temp. 100° C.	60	5.62	14.37	19.99	28.1	1373	71.9	0.00984
	120	9.53	10.06	19.59	48.7	1352	51.3	0.01064
	180	13.26	7.51	20.77	63.8	1337	36.2	0.01140
	240	Flask broke						
	300	14.78	3.69	18.47	80.0	1321	20.0	0.00984
	360	16.46	2.79	19.25	85.5	1316	14.5	0.00989
Average constant = 0.0100	420	14.30	1.96	16.26	87.9	1313	12.1	0.00932
	480	31.48	2.93	34.41	91.5	1310	8.5	0.01046

Paranitrobenzamide.

	60	6.11	12.62	18.73	32.6	1368	67.4	0.0117
	120	11.02	9.10	20.12	54.5	1347	45.5	0.0119
	180	14.00	6.26	20.26	69.1	1332	30.9	0.0119
	240	17.80	4.86	22.66	78.6	1322	21.4	0.0118
	300	14.20	2.46	16.66	85.2	1316	14.8	0.0117
	360	16.18	1.89	18.07	89.6	1311	10.4	0.01165
Average constant = 0.0118	420	Sample lost						
	480	19.57	1.01	20.58	95.1	1306	4.9	0.0117

Series VII.

$H_2SO_4 = A = 0.2851$ N. $B = 0.04026$ N. $A-B = 0.2448$. $A/B = 7.07$. Standard $H_2SO_4 = 0.1419$ N.

Metanitrobenzamide.

	t.	Changed.	Unchanged.	Total.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	60	2.92	15.79	18.71	15.6	691	84.4	0.00989
March 8, 1897	120	5.40	13.90	19.30	28.0	679	72.0	0.00975
	180	4.47	11.76	19.23	38.8	669	61.2	0.00983
Temp. 100.36° C.	240	9.45	10.60	20.05	47.1	660	52.9	0.00964
	300	11.02	9.41	20.43	53.8	653	46.2	0.00942
	360	11.20	7.57	18.77	59.7	647	40.3	0.00930
Average constant = 0.0095	420	12.17	6.63	18.80	64.7	642	35.3	0.00905
	480	22.58	9.94	32.52	69.4	638	30.6	0.00919

Paranitrobenzamide.

	60	3.81	18.65	22.46	17.0	690	83.0	0.0109
March 10, 1897	120	5.44	12.77	18.21	29.9	677	70.1	0.0105
Bar. 752.7	180	8.03	11.62	19.65	40.9	666	59.1	0.0105
Temp. 99.7° C.	240	10.14	10.07	20.21	50.2	657	49.8	0.0106
	300	11.19	8.44	19.63	57.0	650	43.0	0.01035
	360	11.53	6.57	18.10	63.7	643	36.3	0.0104
Average constant = 0.0105	420	13.28	5.80	19.08	69.6	637	30.4	0.0105
	480	22.40	7.82	30.22	74.1	633	25.9	0.0105

EXPERIMENTS.—GROUP II.

Hydrolysis of o-, m-, and p-Nitrobenzamides with Alkalies.

Heating the Amides.—The arrangement of the flask in which the hydrolysis was carried on was exactly the same as above described except that the air which was blown into the upright tube was made to pass over soda-lime, and the upright tube was not jacketed with water in the experiments carried on below the boiling temperature. The same water-bath, as above, was used at boiling, but for carrying on the reaction at lower temperatures the flasks were suspended in a large thermostat. This consisted of a tin boiler about 50 cm. by 25 cm. by 40 cm. deep, containing about 40 liters of water. This was heated by a double gas-stove, fed through a large Ostwald gas-regulator of special construction. Much trouble was caused by the frequent breaking of the large glass bulb which contained the solution of calcium chloride until the glass bulb was replaced by a brass tube about 25 mm. in diameter and about 70 cm. in length containing 300 cc. of solution. It was so bent as to extend nearly around the bath several centimeters from the walls and about 7 centimeters from the bottom. A small brass tube some 6 mm. in diameter was brazed into one end. This was bent up vertically and then over the edge of the bath, and was connected with the gas-regulator by means of a firm rubber joint. Instead of providing for a constant supply of gas through the regulator, as is customary, two small "pilot" flames, supplied from an independent source, were placed beside the two stove burners.

The tin boiler was covered with thick asbestos board, and was kept filled to a certain level by being connected through a syphon with a tin vessel containing about 800 cc. of water which was kept within 1° or 2° of the temperature of the bath, by a Bunsen burner controlled by a small Ostwald gas-regulator. This vessel was kept filled by a constant level attachment.

The water in the bath was kept well stirred by a stirrer driven by a water motor. No considerable difference of temperature could be noted in the various parts of the bath.

When the brass tube was filled with an ordinary solution of

calcium chloride, the temperature of the bath when set at 80° or 90° C. was found to sink gradually. This was finally traced to the air originally dissolved in the water from which the solution was made. This air gradually separates out when the bath is kept at a high temperature, and causes the regulator to shut off the gas at too low a temperature. This difficulty was entirely overcome by boiling the solution vigorously and cooling it in a vacuum, and also boiling it in the tube during the filling.

A thermometer, found to read 0.40° C. too high at 100° C. and 0.80° C. too high at 0° C. and having a scale about 40 cm. long extending from 0° to 100° C. on which hundredths could be easily estimated, was kept suspended in the bath and was read from 30 to 70 times during each experiment while the amides were in the bath. At 80°C. or below, the extreme variation could be kept within about 0.1° C., while at 90° C. it was usually about 0.2° C.

Analysis of Samples.—Since the reaction

$$R—CONH_2 + KOH = R—COOK + NH_3,$$

involves the elimination of ammonia which is liable to escape from the alkaline solution, the amount of hydrolysis cannot be determined directly as in the preceding cases. The method adopted was to put the sample in the distilling-flask with magnesium hydroxide and to distil off all ammonia until the distillate came over neutral. Then only, was a receiver with standard acid connected with the condenser and caustic soda run into the distilling-flask to decompose the residual amide and drive over the resulting ammonia. This was titrated in the usual manner. But to determine the per cent of decomposition the total amide must be known. As the same amount of amide was always put into the same amount of solution, this could be readily calculated from the volume of the sample which was found as follows: A 100 cc. measuring-flask was carefully dried and 10.0 cc. of a solution containing 0.5 gram magnesium sulphate per cc. or, when the alkali used was barium hydrate, an equivalent amount of magnesium chloride, measured in from a burette. The sample was blown into this in the usual manner. The caustic alkali of the re-

acting solution is immediately rendered harmless by double decomposition with the magnesium salt. The measuring-flask was then placed in cold water until it had reached the temperature of the room, when it was filled with water from a burette. The capacity of each measuring-flask used was determined by measuring into it the same amount of the magnesium salt solution and filling up to the mark with an alkaline solution of the same strength as that used in the experiments. In this way any error due to the precipitation of the magnesium hydroxide was avoided. To get the volume of each sample it was only necessary to subtract from this figure the amount of water required to fill the flask to the mark +10.0 cc., the amount of the magnesium salt solution which had previously put in. Found in this way the volume of the sample was considered correct to a tenth of a cubic centimeter or to about one part in seven hundred, which was accurate enough, considering other sources of error.

For convenience in calculating results a table was made out, giving for each tenth of a cubic centimeter of the reacting solution, from 65.0 cc. up to 85.0 cc., the volume of standard acid, 0.1433 N., corresponding to the original content of amide.

The caustic potash and caustic soda solutions used, were titrated against standard acid using phenolphthalein and methyl-orange as indicators, in order to determine the amount of carbonate present. This rarely amounted to more than 1 per cent of the whole and was disregarded. The caustic soda was in some cases prepared from the metal in water and in others from a solution of the sulphate and barium hydrate. The following tables give the results. In all cases two flasks the one containing the meta- and the other para-amide, were heated in the same bath.

Series I.

NaOH = A = 0.08824 N. B = 0.04026. $A-B$ = 0.04798. A/B = 2.192. Standard H_2SO_4 = 0.1419 N. March 17, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Sample. cc.	Total cc. acid.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	6.72	68.7	19.59	65.8	153.4	34.2	0.499
	60	3.24	82.4	23.48	86.1	133.1	13.9	0.502
Temp. 100.34° C.	90	1.32	73.2	20.59	93.6	125.0	6.4	0.509
	120	0.63	81.8	23.31	97.3	121.9	2.7	0.523
	150	0.27	81.1	23.12	98.4	120.8	1.6	0.489
	180	0.23	73.3	20.92	98.9	120.3	1.1	0.452
Average constant = 0.496	210		73.7		Were thought to contain too little ammonia for analysis.			
	240		19.9					

Paranitrobenzamide.

	30	4.62	61.20	17.46	73.1	146.1	26.9	0.629
	60	1.34	43.70	12.46	89.2	130.0	10.8	0.590
	90	1.04	79.4	22.55	95.3	123.9	4.7	0.576
	120	0.51	73.0	20.82	97.5	121.7	2.5	0.538
	150	0.28	70.7	20.15	98.6	120.6	1.4	0.509
	180	0.15	69.6	19.85	99.2	120.0	0.8	0.489
Average constant = 0.555	210		70.8		Were thought to contain too little ammonia for analysis.			
	240		84.4					

Series II.

NaOH = B = 0.01896 N. A = 0.04026 N. $A-B$ = 0.02130. A/B = 2.123. Standard H_2SO_4 = 0.1419 N. March 30, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Equiv. of amide in sample.	Per cent changed, x.	$A-x$.	$B-x$.	K.
Temp. of boiling water	20	15.30	64.5	8.62	18.30	34.8[1]	177.5	65.2	0.584
	40	16.10	72.9	9.97	16.10	47.0	165.3	53.0	0.452
	60	15.43	74.0	9.89	21.19	56.2	156.1	43.8	0.405
	80	15.54	79.5	10.62	22.66	66.0	146.3	34.0	0.410
	100	15.30	81.0	10.82	23.09	70.9	141.4	29.1	0.381
	120	13.23	73.0	9.75	20.80	76.7	135.6	23.3	0.395
Average constant = 0.409	140	13.64	77.2	10.31	22.00	79.9	132.4	20.1	0.379
	160	9.18	51.7	6.91	14.73	79.5	132.8	20.5	Sample too small

Paranitrobenzamide.

	20	15.97	67.0	8.95	19.09	34.0	178.3	66.0	0.565
	40	16.06	76.1	10.17	21.69	54.4	157.9	45.6	0.574
	60	13.50	68.4	9.14	19.49	64.7	147.6	35.3	0.532
	80	14.18	76.1	10.14	21.60	72.9	139.4	27.1	0.507
	100	12.57	71.6	9.57	20.41	80.9	131.4	19.1	0.552
	120	12.53	72.4	9.67	20.63	82.8	129.5	17.2	0.495
Average constant = 0.531	140	11.20	65.9	8.80	18.78	85.2	127.1	14.8	0.468
	160	13.02	79.0	10.55	22.51	89.0	123.3	11.0	0.558

[1] In Series II the percentages were calculated from the amount of alkali that became neutralized in the experiment, as the amide was in excess.

Series III.

NaOH $= A =$ ρ.06497. $B = 0.4026$. $A-B = 0.02471$. $A/B = 1.614$. Standard HCl = 0.1433 N. April 27, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	11.96	72.6	20.39	41.4	120.0	58.6	0.321
90.0° C.	60	7.35	66.5	18.68	60.7	100.7	39.3	0.312
	90	5.00	63.1	17.73	71.8	89.6	28.2	0.304
	120	4.82	72.2	20.28	76.2	85.2	23.8	(0.268)
	150	2.88	67.3	18.91	84.8	76.6	15.2	0.307
	180	2.20	64.2	18.03	87.8	73.6	12.2	0.296
Average constant = 0.305	210	1.97	76.1	21.38	90.8	70.6	9.2	0.300
	240	1.68	84.0	23.60	92.9	68.5	7.1	0.301

Paranitrobenzamide.

	25	10.63	65.7	18.46	42.4	119.0	57.6	0.400
	60	5.89	63.2	17.75	66.8	94.6	33.2	0.392
	90	4.46	71.9	20.20	77.9	83.5	22.1	0.382
	120	3.28	74.0	20.79	84.2	77.2	15.8	0.374
	150	2.56	81.6	22.92	88.8	72.6	11.2	0.375
	180	1.65	70.4	19.78	91.7	69.7	8.3	0.371
Average constant = 0.376	210	1.05	58.9	16.55	93.7	67.7	6.3	0.365
	240	0.32	22.2	6.24	94.9	66.5	5.1	0.352

SERIES IV.

NaOH = A = 0.06734 N. B = 0.04026 N. $A-B$ = 0.02708. A/B = 1.670. Standard HCl = 0.1433 N. May 4, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	14.05	67.8	19.04	26.2	140.8	73.8	(0.105)
80.03° C.	60	14.35	82.8	23.35	38.3	128.7	61.7	(0.140)
Av. of 70 readings	90	9.38	78.7	22.11	57.6	109.4	42.4	0.179
Total var. 0.12° C.	120	6.34	69.2	19.44	67.4	99.6	32.6	0.186
	150	5.08	65.1	18.29	72.2	94.8	27.8	0.176
	180	4.28	69.5	19.52	78.1	88.9	21.9	0.182
Average constant = 0.184	210	3.69	73.0	20.50	82.0	85.0	17.0	0.193
	240	3.23	78.6	22.08	85.4	81.6	14.6	0.187

Paranitrobenzamide.

	30	12.91	70.3	19.75	34.6	132.4	65.4	0.237
NaOH made from Na_2SO_4 and	60	9.26	70.0	19.66	52.9	114.1	47.1	0.229
$Ba(OH)_2$	90	5.70	57.7	16.21	64.8	102.2	35.2	0.227
	120	4.42	57.0	16.01	72.4	94.6	27.6	0.221
	150	3.69	62.9	17.67	79.1	87.9	20.9	0.227
	180	3.71	77.8	21.86	83.0	84.0	17.0	0.223
Average constant = 0.223	210	2.71	66.3	18.63	85.4	81.6	14.6	0.213
	240	2.88	87.8	23.55	87.8	79.2	12.2	0.209

Series V.

NaOH = A = 0.06923 N. B = 0.04026 N. $A-B$ = 0.02897. A/B = 1.720. Standard HCl = 0.1433 N. May 7, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
70.07° C.	30	18.76	80.8	22.70	17.3	154.7	82.7	(0.097)
34 readings	60	13.21	67.1	18.85	28.7	143.3	71.3	(0.090)
Maximum var. 0.08° C.	90	11.94	75.6	21.24	43.8	128.2	56.2	0.108
	120	8.87	65.0	18.25	51.4	120.6	48.6	0.106
	150	8.66	74.5	20.93	58.5	113.5	41.5	0.109
	180	7.27	71.0	19.95	63.6	108.4	36.4	0.105
Average constant = 0.107	210	6.12	68.1	19.13	68.0	104.0	32.0	0.105
	240	4.33	68.9	19.36	71.9	100.1	28.1	0.107

Paranitrobenzamide.

	30	13.55	69.6	19.55	12.8	159.2	87.2	(0.067)
NaOH made from Na_2SO_4 and $Ba(OH)_2$	60	11.73	67.5	18.96	28.1	143.9	71.9	(0.087)
	90	11.12	72.8	20.45	45.6	126.4	54.4	0.115
	120	8.34	61.3	17.22	53.9	118.1	46.1	0.114
	150	4.73	42.4	11.91	60.3	111.7	39.7	0.113
	180	5.86	62.5	17.56	66.6	105.4	33.4	0.116
Average constant = 0.114	210	5.45	61.4	17.25	69.1	102.9	30.9	0.109
	240	5.33	74.8	21.02	74.6	97.4	25.4	0.115

Series VI.

NaOH = A = 0.06798 N. B = 0.04026 N. $A-B$ = 0.02772 N. A/B = 1.688. Standard HCl = 0.1433 N. May 17, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
59.98° C.	30	13.75	54.7	15.39	10.7	158.1	89.3	0.0573
Average of 29 readings	60	16.31	72.9	20.48	20.4	148.4	79.6	0.0597
Max. var. 0.2° C.	90	13.86	68.4	19.22	27.9	140.9	72.1	0.0586
	120	14.91	80.6	22.64	34.1	134.7	65.9	0.0576
	150	11.66	69.2	19.44	40.0	128.8	60.0	0.0579
	180	11.85	77.8	21.85	45.8	123.0	54.2	0.0560
Average constant = 0.0584	210	11.48	81.2	22.81	49.7	119.1	50.3	0.0581
	240	10.86	83.8	23.54	53.8	115.0	46.2	0.0584

Paranitrobenzamide.

	30	15.61	57.4	16.12	3.4	165.4	96.6	(0.0179)
NaOH made from Na_2SO_4 and $Ba(OH)_2$	60	19.69	74.5	20.83	4.0	164.8	96.0	0.0101
	90	17.85	66.6	18.71	4.6	164.2	95.4	0.0078
	120	18.69	71.6	20.11	7.1	161.7	92.9	0.0092
	150	19.47	75.3	21.15	8.4	160.4	91.6	0.0088
	180	16.25	76.2	21.41	Distillation not complete			
Average constant = 0.0091	210	18.26	73.2	20.56	11.2	157.6	88.8	0.0086
	250	22.03	90.6	25.45	13.4	155.4	86.6	0.0100

Series VII.

NaOH[1] = A = 0.06798 N. B = 0.04026 N. $A-B$ = 0.02772 N. A/B = 1.688. Standard HCl = 0.1433 N. May 25, 1897.

Metanitrobenzamide.

	t	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
Temp. 100° C.	30	8.42	67.7		55.7	113.1	44.3	0.497
	60	Sample lost						
Average constant = 0.484	90	3.05	73.4	20.62	85.1	83.7	14.9	0.482
	120	1.83	68.5	19.24	90.4	78.4	9.6	0.474

Paranitrobenzamide.

	30	7.16	64.9	18.23	60.7	108.1	39.3	0.587
	60	3.69	65.1	18.29	79.8	89.0	20.2	0.576
Average constant = 0.572	90	2.11	63.9	17.95	88.2	80.6	11.8	0.562
	120	1.72	88.3	24.80	93.1	75.7	6.9	0.562

[1] Sodium hydroxide made from sodium sulphate and barium hydroxide.—Temperature of boiling water.

Series VIII.

KOH = A = 0.06738 N. B = 0.04026 N. $A-B$ = 0.02712 N. A/B = 1.673. Standard HCl = 0.1433 N. May 28, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
90° C.	30	12.04	71.1	19.97	39.7	127.6	60.3	0.289
	60	8.02	73.4	20.64	61.1	106.2	38.9	0.301
Average of 79 readings 90.03°	90	5.20	66.6	18.74	72.3	95.0	27.7	0.295
Max. var. 0.29° C.	120	4.13	74.1	20.82	80.2	87.1	19.8	0.297
	150	3.28	78.5	22.05	85.1	82.2	14.9	0.293
	180	2.36	73.2	20.56	88.5	78.8	11.5	0.289
Average constant = 0.291	210	1.94	76.7	21.55	91.0	76.3	9.0	0.285
	240	1.52	76.6	21.52	92.5	75.8	7.5	0.276

Paranitrobenzamide.

	30	10.65	71.9	20.20	47.3	120.0	52.7	0.379
	60	6.56	72.3	20.31	67.7	99.6	32.3	0.376
KOH from K_2SO_4 and $Ba(OH)_2$	90	4.58	74.3	20.87	78.1	89.2	21.1	0.380
	120	3.20	76.8	21.57	85.2	82.1	14.8	0.368
	150	2.54	79.0	22.19	88.6	78.7	11.4	0.348
	180	1.77	76.3	21.43	91.7	75.6	8.3	0.347
Average constant = 0.359	210	1.12	62.8	17.64	93.7	73.6	6.3	0.341
	240	0.78	57.4	16.12	95.2	72.1	4.8	0.337

Series IX.

KOH = A = 0.06947 N. B = 0.04026 N. $A-B$ = 0.02921 N. A/B = 1.725. Standard HCl = 0.1433. June 2, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
80° C.	30	14.33	72.4	20.34	29.5	146.0	70.5	0.209
	60	10.35	70.4	19.78	47.7	124.8	52.3	0.185
Average of 50 readings 79.97° C.	90	7.98	68.8	19.33	58.7	113.8	41.3	0.178
Max. var. = 0.16° C.	120	6.57	71.4	20.06	67.2	105.3	32.8	0.177
	150	5.08	70.8	19.89	74.5	98.0	25.5	0.183
	180	4.46	74.6	20.96	78.7	93.8	21.3	0.178
Average constant = 0.182	210	3.81	74.5	20.93	81.8	90.7	18.2	0.173
	240	2.70	64.1	18.01	85.0	87.5	15.0	0.174

Paranitrobenzamide.

	30	12.88	69.7	19.58	34.2	138.3	65.8	0.225
	60	11.17	85.8	24.10	53.7	118.8	46.3	0.226
KOH made from K_2SO_4 and $Ba(OH)_2$	90	7.02	70.8	19.89	64.7	107.8	35.3	0.217
	120	4.73	61.5	17.28	72.6	99.9	27.4	0.214
	150	4.01	66.5	18.68	78.5	94.0	21.3	0.212
	180	3.65	76.1	21.38	82.9	89.6	17.1	0.211
Average constant = 0.216	210		73.7	20.71	Sample not analyzed.			
	240	1.91	63.9	17.95	89.4	83.1	10.6	0.214

Series X.

$Ba(OH)_2 = A = 0.06659$ N. $B = 0.04026$ N. $A - B = 0.02633$ N. $A/B = 1.654$. Standard HCl = 0.1433 N. June 7, 1897.

Metanitrobenzamide.

	t.	Unchanged.	Vol. of Sample.	Equiv. of Sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
90° C.	30	11.61	69.9	19.64	40.9	124.5	59.1	0.305
	60	7.83	81.9	23.00	66.0	99.4	34.0	0.360
47 readings	90	4.77	72.0	20.22	76.4	89.0	23.6	0.348
Variation about 0.3° C.	120	3.76	88.5	22.05	83.0	82.4	17.0	0.340
	150	2.58	75.8	21.30	87.9	77.5	12.1	0.343
	180	1.97	74.3	20.87	90.6	74.8	9.4	0.331
Average constant = 0.336	210	1.47	73.9	20.71	92.9	72.5	7.1	0.229
	240	0.87	59.4	16.73	94.8	70.6	5.2	0.333

Paranitrobenzamide.

	30	10.81	78.3	22.00	50.9	114.5	49.1	0.445
	60	5 87	73.3	20.57	71.5	93.9	28.5	0.436
	90	4.00	73.1	20.53	80.5	84.9	19.5	0.408
	120	2.44	68.7	19.30	87.4	78.0	12.6	0.417
	150	2.03	77.8	21.86	90.7	74.7	9.3	0.400
	180	1.35	75.8	21.30	93.7	71.7	6.3	0.407
Average constant = 0.409	210	0.93	65.7	18.46	95.0	70.4	5.0	0.387
	240	0.79	79.3	22.27	96.4	69.0	3.6	0.389

Series XI.

$Ba(OH)_2 = A = 0.06772$ N. $B = 0.04026$ N. $A-B = 0.02746$. $A/B = 1.682$. Standard HCl = 0.1433 N. June 10, 1897.

Metanitrobenzamide.

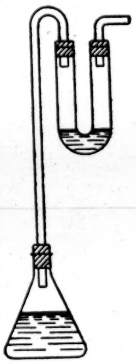
	t.	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
80° C.	30	14.00	73.8	20.73	32.5	135.7	67.5	0.216
	60	10.02	72.4	20.34	50.8	117.4	49.2	0.214
68 readings	90	8.02	74.6	21.05	61.9	106.3	38.1	0.205
Max. var. 0.18° C.	120	6.41	77.8	21.86	70.7	97.5	29.3	0.207
	150	4.62	68.1	19.13	75.8	92.4	24.2	0.199
	180	3.99	72.9	20.48	80.1	88.1	19.9	0.195
Average constant = 0.204	210	3.03	67.2	18.88	84.0	84.2	16.0	0.198
	240	2.65	71.6	20.11	86.8	81.4	13.2	0.197

Paranitrobenzamide.

	30	13.03	73.3	20.59	36.7	131.5	63.3	0.257
	60	9.15	76.5	21.49	57.4	110.8	42.6	0.264
	90	7.09	79.5	22.33	68.2	100.0	31.8	0.253
	120	4.66	72.3	20.31	77.1	91.1	22.9	0.261
	150	3.76	69.9	19.64	80.9	87.3	19.1	0.242
	180	3.06	73.8	20.73	85.2	83.0	14.8	0.243
Average constant = 0.250	210	2.10	62.5	17.56	88.0	80.2	12.0	0.239
	240	2.04	77.3	21.71	90.6	77.6	9.4	0.241

Experiments on o-Nitrobenzamide with Caustic Soda at about 100° C.

It was found impossible to estimate *o*-nitrobenzamide by distilling off the ammonia from it with caustic soda, as was done with the meta- and paranitrobenzamides. This rendered it necessary to retain all the ammonia liberated by the caustic soda during the reaction. To accomplish this the following method was used: 500 mg. of *o*-nitrobenzamide were weighed into a small Erlenmeyer flask and 75 cc. of the caustic soda solution measured in. The flask was closed by a rubber stopper carrying a tube some 30 cm. long, bent over at the top and passing through the stopper of a U-tube containing more than enough acid to neutralize the amount of alkali in the flask. The flask was plunged into boiling water and shaken so as to bring the contents to the required temperature as quickly as possible. At the proper time the flask was removed and shaken in cold water to stop the reaction. By tilting the flask when this was done it could be made to suck back much of the acid in the U-tube. The contents of the flask and the U-tube, together with the washings of both, were placed in a distilling-flask and, after neutralization, the magnesium hydroxide mixture added and the ammonia distilled off in the usual way. The number of cubic centimeters of standard acid neutralized was divided by the volume of standard acid equivalent to 500 mg. of *o*-dinitrobenzamide, to obtain the per cent.



The following table gives the results of a series of four experiments made in this way. The four Erlenmeyer flasks were heated together in the same water-bath, and the temperature considered to be 100° C.

o-Nitrobenzamide.

NaOH = A = 0.06734 N. B = 0.04026 N. $A-B$ = 0.02708. A/B = 1.670. Standard HCl = 0.1433 N. May 4, 1897.

t.	Changed.	Weight of amide. mg.	Equiv. of amide.	Per cent. changed, x.
60	1.98	500	21.07	8.1
125	4.21	"	"	20.0
185	5.34	"	"	25.3
245	6.03	"	"	28.6

EXPERIMENTS.—GROUP III.

Hydrolysis of Several Amides with Hydrochloric Acid at the Temperature of Boiling Water.

o-, *m-*, and *p-Nitrobenzamides; o-*, *m-*, and *p-Amidobenzamides; o-* and *p-Chlorbenzamides; m-* and *p-Brombenzamides; o-Iodobenzamide; o-*, *m-*, and *p-Toluic amides; o-Hydroxybenzamide; o-Methoxybenzamide; o-Ethoxybenzamide.*

Method of Taking Samples.—The method of heating the amide with the acid was the same as in Group I. The hydrochloric acid was made up by measuring 100 cc. of c. p. concentrated hydrochloric acid into a two-liter bottle and diluting to a mark near the neck. An acid of about 0.55 N was obtained. From each bottle full, so made up, 600 cc. were measured into each of the three flasks, which were heated at the same time in the same bath. The strength of the acid was found each time by titrating a portion of the remainder with standard caustic potash.

With many of the amides experimented upon, especially those of the ortho series, it was found impossible to determine the undecomposed amide in the samples as was done with the meta- and paranitrobenzamides in the experiments of Group I. Therefore, as in Group II, it was necessary to know the volume of the sample taken. To this end a 200-cc. measuring-flask was taken, rinsed well with water and then with alcohol, warmed, and dried. Into the flask was measured from a burette 4.5 cc. of a solution containing 0.25 gram caustic soda in each cc. A 100-cc. "full" pipette was filled to the mark and also emptied into the flask, into which the sample

was blown as the seconds hand of the watch passed the 60 seconds mark. The force with which the sample was blown in thoroughly mixed it with the water and alkali in the flask. The 4.5 cc. of caustic soda solution used was sufficient to neutralize 50 cc. of the reacting solution. By mixing with the cold water the temperature was immediately brought down to about 50° or 60° C. The flask was put into cold water, where it was allowed to remain ten minutes, being usually shaken several times in that interval, taken out and filled with water from a burette, which, to avoid mistakes, was filled each time to the zero mark. To lessen errors, the water from the pipette and from the burette was allowed to flow with as nearly as possible the same velocity each time. The burette was usually read twice. The measuring flask was emptied into the proper one of a row of 300 cc. Erlenmeyer flasks and washed twice into the same. As 3 flasks containing the reacting mixtures were heated at the same time, this cycle of operations had to be gone through with for each of the 3 flasks every thirty minutes. In the first few series it was not always possible to get ready for a sample at the proper time. In this event the sample was taken several minutes later and the actual time recorded.

Each of the measuring flasks used was calibrated for this special use by drying, measuring in the 4.5 cc. caustic soda solution, and the contents of the 100-cc. pipette, and filling to the mark from the burette.

Analysis of Samples.—The sample with 10 cc. of the solution of magnesium sulphate added was emptied into the distilling flask and washed twice into the same. It was nearly neutralized with caustic soda, and finally 2 to 2.5 cc. of a solution of the same, 0.25 gram in 1 cc., added. Instead of taking the trouble and time to neutralize the acid, the amount of the caustic soda solution necessary to neutralize the acid and set free the proper amount of magnesium hydroxide was calculated from the known volume of the sample and that amount added, at once, from a burette.

The ammonia was distilled off with steam, caught in the proper amount of standard acid, and titrated as usual. The amount of standard acid neutralized was divided by the vol-

ume of standard acid equivalent to the amide contained originally in the known volume of the sample taken.

In all titrations cochineal was used as indicator. Some solutions made from the same lot of bugs worked splendidly, while for no known reason others were bad and had to be thrown away. The solution seems to deteriorate after about ten days.

From about the fourth series on, all of the water used for making up the acid, for putting in the measuring flasks, etc., and wherever else it was to go into the distilling flask, was distilled from sulphuric and chromic acids.

The results of the experiments made according to this procedure are given in the following tables. An amount of each amide equivalent to 4.000 grams nitrobenzamide was weighed into each flask, except in several cases where the amide was scarce, and in some experiments with difficultly soluble amides, when half that concentration was used :

SERIES I.

Conc. of HCl $= A = 0.5769$ N. Conc. of amide $= B = 0.04026$ N. $A - B = 0.5366$. $A/B = 14.33$. Dec. 15, 1897.

m-Amidobenzamide, $C_6H_4\begin{cases}CONH_2\\NH_2.H_2O\end{cases}$, *3.712 grams.*

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*−*x*.	*B*−*x*.	*K*.
	30	6.25	86.1	24.36	25.6	1407	74.4	0.0172
	63½	12.79		27.31	48.6	1384	51.4	0.0178
	90	14.38	85.9	24.14	59.6	1473	40.4	0.0179
	120	15.66	80.5	22.61	69.3	1364	30.7	0.0176
	150	13.92	63.1	17.73	78.5	1355	21.5	0.0184
	180	18.10	78.5	22.05	82.1	1351	17.9	0.0172
Average constant = 0.0177	210	17.13	69.2	17.13	88.1	1345	11.9	0.0183
	240	13.39	51.4	14.64	91.5	1342	8.5	0.0171

NOTE.—The same concentrations, etc., apply to the tables for *p*-amidobenzamide and benzamide. All were heated at the same time.

SERIES I.—Continued.

p-Amidobenzamide, 3.280 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.
	30	6.12	81.8	22.97	26.6	1406	73.4	0.0180
	66¼	10.18	72.0	20.22	50.3	1383	49.7	0.0187
	94	12.67	71.1	19.97	63.4	1370	36.6	0.0190
	120	15.47	75.3	21.16	73.0	1360	27.0	0.0195
	150½	15.88	69.0	19.38	81.8	1351	18.2	0.0204
Titrations bad	180	16.80	67.0	19.07	88.6	1344	11.4	0.0218
	210	18.15	70.51	19.81	91.6	1341	8.4	0.0214

Benzamide, 2.917 grams.

	40	8.41	82.0	23.03	36.5	1397	63.5	0.0200
	69	13.40	86.4	24.27	55.2	1378	44.8	0.0206
	93	14.97	80.9	22.72	65.9	1367	34.1	0.0211
	122	12.72		17.16	74.1	1359	25.9	0.0210
	151	18.68	80.4	22.58	82.7	1350	17.3	0.0209
	180	19.44	78.0	21.91	88.7	1344	11.3	0.0219
Average constant = 0.0209	211	13.06		14.14	92.4	1341	8.6	0.0211

SERIES II.

HCl = A = 0.5538 N. B = 0.04026 N. $A-B$ = 0.5135. A/B = 13.75. Standard HCl = 0.1433 N. Dec. 17, 1897.

m-Brombenzamide, 4.816 grams.

t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
30	4.81	73.6	20.65	23.3	1352	76.7	0.0161
60	8.70	68.4	19.22	44.2	1331	55.8	0.0179
90	10.88	64.2	18.03	60.3	1315	39.7	0.0190
120	14.38	72.1	20.25	71.0	1304	29.0	0.0192
150	16.72	74.6	20.96	79.8	1295	20.2	0.0200
180	19.31	80.9	22.72	85.0	1290	15.0	0.0199
210	18.89	75.4	21.18	89.2	1286	10.8	0.0179
240	Volume of sample lost.						

Average constant = 0.0184

NOTE.—Great difficulty was experienced in getting the amides in solution. The insolubility of the acids formed seemed to cause irregularities.

Series II.—Continued.

p-Brombenzamide, 4.816 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.
	30	3.38	58.2	16.35	20.7	1354	79.3	0.0140
	60	6.45	56.0	15.73	41.0	1334	59.0	0.0161
	90	10.52	69.9	19.67	53.6	1321	46.4	0.0157
	120	13.69	77.3	21.71	63.1	1312	36.9	0.0154
	150	12.30	63.2	17.75	69.3	1306	30.7	0.0147
	180	13.36	63.9	17.95	74.4	1301	25.6	0.0141
Average constant = 0.0146	210	14.32	65.3	18.35	78.0	1297	22.0	0.0135
	240	15.36	67.2	18.88	81.3	1294	18.7	0.0131

p-Chlorbenzamide, 3.744 grams.

	30	5.22	74.4	20.90	25.0	1350	75.0	0.0170
	60	8.11	64.6	18.15	44.7	1330	55.3	0.0181
	90	10.43	63.0	17.70	58.9	1316	41.1	0.0183
	120	14.57	75.3	21.16	68.6	1308	31.4	0.0180
	150	14.90	70.2	19.72	75.5	1300	24.5	0.0175
	180	Results lost.						
Average constant = 0.0179	210	18.22	73.9	20.74	87.8	1287	12.2	0.0189
	240	14.16	56.7	15.93	88.8	1286	11.2	0.0172

Series III.

HCl = A = 0.5451 N. B = 0.04026 N. $A-B$ = 0.5048. A/B = 13.54. Bar. 757.4 cor.
Hence b. p. of water = 99.9° C. Standard HCl = 0.1433.

o-Toluic Amide, 3.256 grams.

t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
30	0.76	73.7	20.71	3.7	1350	96.3	0.00229
60	1.50	74.8	21.02	7.1	1347	92.9	0.00226
90	2.57	90.4	25.39	10.1	1344	89.9	0.00218
120	2.56	66.6	18.71	13.7	1340	86.3	0.00211
150	3.30	73.7	20.71	15.9	1338	84.1	0.00213
180	3.83	70.4	19.78	19.4	1335	80.6	0.00222
210	3.73	58.9	16.79	22.2	1332	77.8	0.00221
240	4.87	69.3	19.47	25.0	1329	75.0	0.00222

Average constant = 0.00220

NOTE.—Amount of ammonia found in first sample about 1.8 mg. *o*-Amides seem to run little ahead at first or else the analyses are too high, but there is so little ammonia that it is hard to decide this point.

SERIES III.—Continued.

m-Toluic Amide, 3.256 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	4.38	65.0	17.26	25.4	1329	74.6	0.0181
	60	8.76	70.1	19.69	44.5	1310	55.5	0.0183
	90	11.81	70.3	19.75	59.8	1294	40.2	0.0191
	120	13.89	70.1	13.89	70.5	1284	29.5	0.0193
	150	14.98	67.8	19.04	78.7	1275	21.3	0.0196
	180	15.74	66.6	18.71	84.1	1270	15.9	0.0195
Average constant = 0.0193	210	17.17	68.5	19.24	89.2	1265	10.8	0.0204
	240	23.03	89.4	25.11	91.7	1262	8.3	0.0200

p-Toluic Amide, 3.256 grams.

	30	4.81	71.8	20.17	23.8	1330	76.2	(0.0168)
	60	9.13	76.3	21.43	42.6	1311	57.4	0.0173
	90	9.32	59.4	16.74	55.7	1298	44.3	0.0170
	120	12.88	68.4	19.22	67.0	1287	33.0	0.0175
	150	15.93	76.2	21.41	74.4	1280	25.6	0.0172
	180	13.46	58.4	16.41	82.0	1272	18.0	0.0182
Average constant = 0.0175	210	15.68	64.5	18.12	86.5	1268	13.5	0.0176
	240	22.78	88.8(?)	24.95(?)	91.3(?)	1263	8.7	(0.0196)

Series IV.

HCl = A = 0.5538 N. B = 0.4026 N. $A - B$ = 0.5135 N. A/B = 13.75. Standard HCl = 10.433 N. January 4, 1898.

o-Nitrobenzamide, 4.000 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	0.22	66.8	18.77	1.2	1374	98.8	(0.00073)
	60	0.42	68.6	19.27	2.2	1373	97.8	(0.00067)
	90	0.45	65.1	18.29	2.5	1372	97.5	0.00050
	120	0.70	69.5	19.52	3.6	1371	96.4	0.00055
	150	0.99	74.3	20.87	4.7	1370	95.3	0.00058
	180	1.00	72.3	20.31	4.9	1370	95.1	0.00050
Average constant = 0.00054	210	1.16	67.0	18.82	6.2	1369	93.8	0.00055
	240	1.66	91.8	25.78	6.5	1369	93.5	0.00051

NOTE.—The fact that the amount of ammonia found was so very small may account for the irregularity in the first two 0.22 cc. (= 0.53 mg. NH_3). In this series and those following ammonia-free water was used.

SERIES IV.—Continued.

o-Amidobenzamide, 3.280 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.
	30	0.59	59.4	16.68	3.5	1372	96.5	(0.00217)
	60	1.20	68.9	19.33	6.2	1369	93.8	0.00194
	90	1.47	61.4	17.25	8.6	1366	91.4	0.00180
	120	1.77	60.0	16.85	10.5	1364	89.5	0.00167
	150	2.46	65.3	18.35	13.4	1362	86.6	0.00174
	180	3.15	69.1	19.41	16.2	1359	83.8	0.00178
Average constant = 0.00178	210	3.53	67.7	19.02	18.6	1356	81.4	0.00178
	240	4.97	86.1	24.19	20.5	1354	79.5	0.00174

o-Hydroxybenzamide, 3.328 grams.

	30	1.41	62.5	17.59	8.0	1367	92.0	(0.00503)
	60	2.63	60.8	17.08	13.7	1361	86.3	0.00445
	90	3.76	66.9	18.80	20.0	1355	80.0	0.00451
	120	4.91	73.4	20.62	23.8	1351	76.2	0.00413
	150	6.18	70.2	19.72	31.4	1344	68.6	0.00460
	180	7.73	79.4	22.30	34.8	1340	65.2	0.00435
Average constant = 0.00437	210	7.18	66.0	18.54	38.8	1336	61.2	0.00429
	240	11.49	95.4	26.80	42.9	1332	57.1	0.00429

SERIES V.

HCl = A = 0.5520 N. B = 0.04026 N. $A-B$ = 0.5117 N. A/B = 13.71. Bar. 757.2 mm. B. P. water 99.9° C. Standard HCl = 0.1433 N. January 6, 1898.

o-Iodobenzamide, 5.944 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	60	0.80	67.5	18.96	4.2	1367	95.8	(0.00130)
	120	1.34	67.5	18.96	7.1	1364	92.9	(0.00119)
	150	1.65	70.8	19.96	8.2	1363	91.8	0.00104
	180	2.03	71.5	20.08	10.1	1361	89.9	0.00108
	210	2.27	70.7	19.84	11.5	1359	88.5	0.00105
	240	2.58	67.6	19.00	13.6	1357	86.4	0.00111
Average constant = 0.00106	270	3.00	73.6	20.68	14.5	1056	85.5	0.00105
	300	3.54	79.1	22.22	16.0	1355	84.0	0.00106

NOTE.—Here again the first or the first and second samples run ahead, but it may be only apparent, as the amount of ammonia is very small.

Series V.—Continued.

o-Chlorbenzamide, 3.744 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*−*x*.	*B*−*x*.	*K*.
	60	1.69	62.6	17.59	9.6	1361	90.4	0.00305
	120	4.12	73.3	20.59	20.0	1351	80.0	0.00339
	150	4.00	61.5	17.28	23.1	1348	76.9	0.00320
	180	4.95	65.9	18.51	26.8	1344	73.2	0.00317
	210	5.52	64.7	18.17	30.3	1340	69.7	0.00315
	240	6.31	64.7	18.17	34.7	1336	65.3	0.00326
Average constant = 0.00321	270	7.55	70.5	19.81	38.1	1333	61.9	0.00327
	300	11.19	97.4	27.36	40.9	1330	59.1	0.00322

o-Hydroxybenzamide, 3.328 grams.

	60	2.71	68.4	19.22	14.1	1357	85.9	(0.00463)
	120	4.97	68.4	19.22	25.9	1345	74.1	(0.00458)
	150	6.17	73.2	20.56	30.0	1341	70.0	0.00432
	180	7.95	81.6	22.92	34.7	1336	65.3	0.00436
	210	7.59	69.5	19.52	38.9	1332	61.1	0.00433
	240	9.39	77.3	21.71	43.3	1328	56.6	0.00439
Average constant = 0.00437	270	8.90	66.9	18.80	47.3	1324	52.7	0.00440
	300	11.59	81.0	22.75	50.9	1320	49.1	0.00440

Series VI.

HCl = A = 0.5557 N. B = 0.04026 N. $A-B$ = 0.5154. A/B = 13.80. B. P. water 100.06° C. January 11, 1898.

m-Nitrobenzamide, 4.000 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	5.28	67.7	18.99	27.8	1352	72.2	0.0197
	60	10.27	77.1	21.66	47.4	1333	52.6	0.0197
	90	15.92	91.7	25.76	61.8	1318	38.2	0.0198
Total variation = 2 per cent.	120	14.04	70.0	19.66	71.4	1309	28.6	0.0194
of constant	150	16.29	73.4	20.62	79.0	1301	21.0	0.0194
	180	15.71	65.7	18.46	85.1	1295	14.9	0.0198
Average constant = 0.0196	210	13.90[1]	53.9	15.14	88.9[2]	1291	11.1	0.0197
	240	21.82[1]	82.6	23.20	91.9[2]	1288	8.1	0.0198

m-Nitrobenzamide (Old Way).

	t.	Changed.	Unchanged.	Total.	Per cent. x.			
	30	5.28	13.65	18.93	27.9	1352	72.1	0.0198
	60	10.27	11.30	21.57	47.6	1332	52.4	0.0197
	90	15.92	9.66	25.58	62.2	1318	37.8	0.0200
	120	14.04	5.54	19.58	71.7	1309	28.3	0.0196
	150	16.29	4.32	20.61	79.0	1301	21.0	0.0194
	180	15.71	2.76	18.47	85.1	1295	14.9	0.0198
Average constant = 0.0197	210	13.90[1]	1.68	15.58[1]	88.9[2]	1291	11.1	0.0197
	240	21.82[1]	1.87	23.69[1]	91.9[2]	1288	8.1	0.0198

[1] Calculated from unchanged amide and total amide in sample.

[2] Some mistake.

SERIES VI.—Continued.

p-Nitrobenzamide, 4.000 grams.

On account of a precipitate which forms on cooling, 0.3 was deducted from the volume of each sample.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*−*x*.	*B*−*x*.	*K*.
	30	6.11	67.1	18.85	32.4	1348	67.6	0.0238
	60	8.84	59.3	16.65	53.9	1326	46.1	0.0237
	90	12.39	64.9	18.23	67.9	1312	32.1	0.0234
	120	13.34	61.1	17.16	77.7	1302	22.3	0.0233
	150	15.99	67.0	18.82	85.0	1295	15.0	0.0237
	180	16.47	65.4	18.37	89.6	1290	10.4	0.0234
Average constant = 0.0236	210	15.72	60.1	16.87	93.2	1287	6.8	0.0242
	240	24.57	92.0	25.83	95.1	1285	4.9	0.0238

Benzamide, 2.917 grams.

	30	5.21	64.6	18.12	28.7	1351	71.3	0.0204
	60	9.91	72.8	20.45	48.5	1332	51.5	0.0203
	90	12.55	70.2	19.72	63.6	1316	36.4	0.0208
	120	14.14	69.1	19.41	72.9	1507	27.1	0.0202
	150	13.69	59.9	16.82	81.4	1299	18.6	0.0210
	180	15.94	67.1	18.85	84.6	1295	15.4	(0.0195)
Average constant = 0.0208	210	18.02	70.8	19.90	90.6	1289	9.4	0.0212
	240	24.21	92.3	25.92	93.4	1287	6.6	0.0214

SERIES VI.—Continued.

The samples of *m*-nitrobenzamide were analyzed according to the method in Group I. also, so that the results could be calculated in both ways in order to compare the two methods. This shows that it is better to calculate the total amide from the volume of the sample.

SERIES VII.

HCl = A = 0.5536 N. B = 0.04026 N. $A-B$ = 0.5133 N. A/B = 13.75. Bar. = 765.9 mm. cor. B. P. water = 100.2° C. Standard HCl = 0.1433 N. January 14, 1898.

o-Ethoxybenzamide, 2.650 grams in 400 cc. of Solution.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	60	5.09	69.3	19.47	26.1	1349	73.9	0.00920
	120	9.12	72.6	20.39	44.7	1330	55.3	0.00907
	180	11.41	67.8	19.04	59.9	1315	40.1	0.00941
	210	11.68	94.0	17.98	64.9	1310	35.1	0.00926
Average constant =	240	12.85	64.9	18.23	70.5	1305	29.5	0.00948
0.00928	370	10.22	46.4	13.04	78.3	1297	21.7	(0.01060)

SERIES VII.—Continued.

o-Methoxybenzamide, 2.426 grams in 500 cc. solution.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.
	60	5.80	66.3	18.63	31.1	1344	68.9	0.0114
	120	7.77	52.2	14.66	53.0	1322	47.0	0.0115
	150	11.71	67.0	18.82	62.2	1313	37.8	0.0120
	180	13.72	71.5	20.08	68.3	1307	31.7	0.0119
	210	10.47	51.5	14.47	72.3	1303	27.7	0.0114
Average constant = 0.0116	240	15.94	77.0	21.63	73.7	1301	26.3	(0.0104)
	270	21.06	93.0	26.12	80.6	1294	19.4	0.0116

o-Toluic Amide, 2.712 grams in 500 cc. solution.

	60	1.36	63.7	17.89	7.5	1368	92.5	0.00236
	120	2.44	61.7	17.33	14.1	1361	85.9	0.00230
	150	3.38	72.1	20.25	16.6	1358	83.4	0.00220
	180	3.47	62.0	17.42	19.9	1355	80.1	0.00224
Previous 0.00220	210	3.84	90.4	16.96	22.6	1352	77.4	0.00222
Average constant =	240	5.70	78.6	22.08	25.9	1349	74.1	0.00228
0.00224	270	6.96	88.8	24.95	27.9	1347	72.1	0.00221

Series VIII.

HCl $= A = 0.5494$ N. $B = 0.02013$ N. $A-B = 0.5293$. $A/B = 26.19$. Bar. 769.8 mm. cor. B. P. water 100.35° C. January 18, 1898.

p-Brombenzamide, 2.408 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	2.65	68.8	9.65	27.5	2592	72.5	0.0196
	60	4.55	69.1	9.70	46.9	2572	53.1	0.0193
	90	5.68	66.2	9.29	61.1	2558	38.9	0.0193
	120	7.08	71.3	10.00	70.8	2548	29.2	0.0189
Previous 0.0146	150	8.22	76.3	10.57	77.7	2541	22.3	0.0185
	180	8.13	71.3	10.00	81.3	2538	18.7	0.0172
Average constant = 0.0185	210	9.24	76.2	10.69	86.4	2533	13.6	0.0176
	240	7.04	55.7	7.82	90.0	2529	10.0	0.0178

Note.—Owing to the fact that they are but slightly soluble, and that their acids are almost insoluble, the first two of these have given so much trouble, that half the usual concentrations were tried. This seems to affect the constant, as seen in the case of *p*-nitrobenzamide, 0.3 cc. on the bromamide, and 0.2 cc. on others, allowed on the volume of sample for precipitation.

SERIES VIII.—Continued.

p-Chlorbenzamide, 3.744 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, *x*.	*A*−*x*.	*B*−*x*.	*K*.
	30	2.52	62.6	8.29	30.4	2589	69.6	(0.0221)
	60	4.60	67.0	9.41	48.9	2570	51.1	0.0205
	90	5.08	57.5	8.04	63.0	2556	37.0	0.0208
	120	6.75	65.7	9.22	73.2	2546	26.8	0.0203
Previous 0.0178	150	8.88	79.2	11.12	79.8	2539	20.2	0.0197
	180	7.11	59.0	8.28	85.9	2533	14.1	0.0202
Average constant = 0.0204	210	9.43	74.8	10.50	90.0	2529	10.0	0.0204
	240	12.21	93.2	13.10	93.2	2526	6.8	0.0209

p-Nitrobenzamide, 4.000 grams.

	30	3.59	74.8	10.57	34.2	2585	65.8	0.0255
	60	4.94	62.7	8.80	56.1	2563	43.9	0.0252
	90	7.16	71.8	10.08	71.0	2548	29.0	0.0254
	120	8.66	76.1	10.68	81.0	2538	19.0	0.0256
	150	8.14	65.0	9.13	89.2	2530	10.8	(0.0276)
	180	7.68	60.4	8.48	90.9	2528	9.1	0.0249
Average constant = 0.0251	210	10.44	78.6	11.04	94.6	2524	5.4	0.0239
	240	12.61	92.6	13.00	97.0	2522	3.0	(0.0274)

Series IX.

HCl = A = 0.5525 N. B = 0.02013. $A-B$ = 0.5324. A/B = 27.49. Bar. 764.5 mm. cor. B. P. water 100.16° C. January 21, 1898.

p-Brombenzamide, 2.408 grams.

t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
30	2.60	68.6	9.63	27.0	2722	73.0	0.0194
60	4.59	71.2	9.99	45.9	2703	54.1	0.0187
90	5.37	68.1	9.56	56.2	2691	43.8	0.0168
120	6.94	71.7	10.06	69.0	2680	31.0	0.0179
150	7.39	69.9	9.81	75.3	2674	24.7	0.0172
180	8.25	74.3	10.43	79.1	2670	20.9	0.0160
210	8.37	80.7	11.32	82.8	2666	17.2	0.0154
240	Distillation not complete.						

Average constant = 0.0173

NOTE.—HCl in Series IX and X not titrated, but this is the usual value, and it is certainly close to the truth.

Series IX.—Continued.

m-Brombenzamide, 2.408 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	2.93	70.2	9.86	29.7	2719	70.3	0.0214
	60	4.73	65.9	9.25	51.1	2698	48.9	0.0218
	90	6.00	65.9	9.25	64.9	2684	35.1	0.0214
	120	7.87	73.5	10.32	76.3	2673	23.7	0.0221
	150	9.07	79.8	11.20	82.8	2666	17.2	0.0217
	180	9.15	73.7	10.38	88.2	2661	11.8	0.0220
Average constant = 0.0210	210	9.35	71.8	10.08	92.7	2656	7.3	0.0231
	240	11.67	87.9	12.34	94.6	2654	5.4	0.0226

p-Chlorbenzamide, 1.872 grams.

	30	2.51	65.5	9.20	27.3	2722	72.7	0.0193
	60	4.25	63.1	8.86	48.3	2701	52.0	0.0199
	90	6.23	71.1	9.98	62.4	2687	37.6	0.0200
	120	7.42	71.8	10.08	73.6	2675	26.4	0.0204
	150	8.99	80.0	11.23	80.1	2669	19.9	0.0199
	180	7.89	65.7	9.23	85.5	2664	14.5	0.0198
Average constant = 0.0196	210	8.54	68.9	9.68	88.2	2661	11.8	0.0188
	240	10.68	82.2	11.54	92.6	2656	7.4	0.0201

Series X.

HCl = A = 0.5525. B = 0.04026 N. $A - B$ = 0.5122. A/B = 13.74. Bar. 752.7 cor. B. P. water 99.73° C.

p-Amidobenzamide, 3.280 grams.

	t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, x.	$A-x$.	$B-x$.	K.
	30	4.31	64.8	19.61	22.0	1352	78.0	(0.0151)
	60	8.58	71.1	19.97	43.0	1341	57.0	0.0175
	90	10.59	66.8	18.77	56.4	1318	43.6	0.0171
	120	12.12	63.9	17.95	66.7	1307	33.3	0.0171
	150	26.28	75.5	21.21	76.8	1297	23.2	0.0183
	180	15.25	66.2	18.60	82.0	1292	18.0	0.0183
Average constant = 0.0177	210	14.02	57.5	16.15	86.8	1287	13.2	0.0182
	240	21.75	83.0	23.31	93.3	1281	6.7	(0.0214)

m-Amidobenzamide, 37.12 grams.

	30	4.31	63.6	17.87	24.1	1350	75.9	0.0167
	60	8.51	70.5	19.84	42.4	1332	57.6	0.0169
	90	10.39	65.1	18.29	56.3	1318	43.7	0.0171
	120	Reading lost						
	150	14.38	69.3	19.47	73.8	1300	26.2	0.0176
	180	16.66	73.9	20.76	80.3	1294	19.7	0.0170
Average constant = 0.0170	210	17.44	72.1	20.25	86.1	1288	13.9	0.0177
	240	Distilling flask broke						

RECAPITULATION.

Constant of Benzamide = 0.0209.

o-Amido.	*o*-Chlor.	*o*-Iodo.	*o*-Nitro.
0.00217	0.00305	0.00130	0.00073
0.00194	0.00339	0.00119	0.00067
0.00180	0.00320	0.00104	0.00050
0.00167	0.00317	0.00108	0.00055
0.00174	0.00315	0.00105	0.00058
0.00178	0.00326	0.00111	0.00050
0.00178	0.00327	0.00105	0.00055
0.00174	0.00322	0.00106	0.00051
0.00178	0.00321	0.00106	0.00054

o-Toluic.	*o*-Toluic.	*o*-Hydroxy.	*o*-Hydroxy.	*o*-Methoxy.	*o*-Ethoxy.
0.00229	0.00236	0.00503	0.00463	0.0114	0.0092
0.00226	0.00230	0.00445	0.00458	0.0115	0.0091
0.00218	0.00220	0.00451	0.00432	0.0120	0.0094
0.00211	0.00224	0.00413	0.00436	0.0119	0.0093
0.00213	0.00222	0.00460	0.00433	0.0114	0.0095
0.00222	0.00228	0.00435	0.00439	(0.0104)	(0.0160)
0.00221	0.00221	0.00429	0.00440	0.0116	....
0.00222	....	0.00429	0.00440	....	....
0.00220	0.00224	0.00437	0.00437	0.0116	0.0093

Group.	Weight.	Constant of benzamide—constant of ortho groups.	Retardation. Per cent.
—CH_3	15	0.0187	89.4
—NH_2	16	0.0191	91.5
—OH	17	0.0164	79.1
—O.CH_3	31	0.0093	44.1
—Cl	35.4	0.0177	84.6
—O.C_6H_5	45	0.0116	55.8
—NO_2	46	0.0204	97.4
—I	127	0.0198	94.9

Summary of Constants.

Benzamide.	Benzamide.	*m*-Nitro.	*p*-Nitro.	½ conc. *p*-Nitro.	*m*-Amido.	*m*-Amido.
0.0200	0.0204	0.0197	0.0238	0.0255	0.0172	0.0167
0.0206	0.0203	0.0197	0.0237	0.0252	0.0178	0.0169
0.0211	0.0208	0.0198	0.0234	0.0254	0.0179	0.0171
0.0210	0.0202	0.0194	0.0233	0.0256	0.0176	....
0.0209	0.0210	0.0194	0.0237	(0.0276)	0.0184	0.0167
0.0219	(0.0195)	0.0198	0.0234	0.0248	0.0172	0.0170
0.0211	0.0212	0.0197	0.0242	0.0238	0.0183	0.0177
....	0.0214	0.0198	0.0238	(0.0275)	0.0171	....
0.0209	0.0208	0.0196	0.0236	0.0256	0.0177	0.0170

p-Amido.	*p*-Amido.	*p*-Chlor.	½ conc. *p*-Chlor.	½ conc. *p*-Chlor.	*m*-Brom.
0.0180	(0.0151)	0.0170	(0.0221)	0.0193	0.0151
0.0187	0.0175	0.0181	0.0205	0.0199	0.0179
0.0190	0.0171	0.0183	0.0208	0.0200	0.0190
0.0195	0.0171	0.0180	0.0203	0.0204	0.0192
0.0204	0.0183	0.0175	0.0197	0.0199	0.0200
0.0218	0.0183	....	0.0202	0.0198	0.0199
0.0214	0.0182	0.0189	0.0204	0.0188	0.0179
....	(0.0214)	0.0172	0.0209	0.0201	....
0.0198	0.0177	0.0179	0.0204	0.0196	0.0184

½ conc. *m*-Brom.	*p*-Brom.	½ conc. *p*-Brom.	½ conc. *p*-Brom.	*m*-Toluic.	*p*-Toluic.
0.0214	0.0140	0.0196	0.0194	0.0181	0.0168
0.0218	0.0161	0.0193	0.0187	0.0183	0.0173
0.0214	0.0157	0.0193	0.0168	0.0191	0.0170
0.0221	0.0154	0.0189	0.0179	0.0193	0.0175
0.0217	0.0147	0.0185	0.0172	0.0196	0.0172
0.0220	0.0141	0.0172	0.0160	0.0195	0.0182
0.0231	0.0135	0.0176	0.0154	0.0204	0.0176
0.0226	0.0131	0.0178	....	0.0200	(0.0196)
0.0210	0.0146	0.0186	0.0173	0.0193	0.0175

DISCUSSION OF RESULTS.

Experiments, Group I.—Series 1, 2, 3, and 4 with hydrochloric acid show very clearly that *o*-nitrobenzamide yields extremely slowly to the action of the acid while the meta is readily hydrolyzed and the para still more so. The constants obtained for the meta and para do not vary specially with different concentrations of the acid. The variations in the constants found may be due to changes of barometric pressure. As a very dilute acid is much more completely dissociated it would be expected to give a higher constant. The ammonium salt formed certainly retards the reaction, comparatively, much more with a weak than with a strong acid. These two opposite effects may balance and keep the actual velocity very nearly the same.

Series 5, 6, and 7 indicate that the relations between the meta- and paranitrobenzamides are approximately the same with sulphuric acid as with hydrochloric acid. The results, though not quite comparable, show that the sulphuric acid is

about 0.45 times as strong as hydrochloric. Should one wish to compare the strengths of acids by measuring the rates at which they hydrolyze a given amide it seems that it would be proper to divide the average constant found in a series with one by the similar average constant found with the other, the conditions under which the measurements were made being the same. Some years ago Ostwald[1] in his elaborate studies on the hydrolysis of acetamide, arbitrarily, as he says, estimated the strengths of a number of acids from the time it took them to hydrolyze 50 per cent of the acetamide.

Experiments, Group II.—In Series I the caustic soda was made by adding sodium to water. The results show a high but decreasing constant. In Series II the alkali was made by adding barium hydrate to an approximately $\frac{N}{10}$ solution of pure sodium sulphate. The large excess of sodium sulphate seems to have retarded the reaction. The slowing up of the reaction due to formation of neutral salts in addition to that already in solution appears also in Series III and IV ; in the latter the metaamide does not seem to have gone into solution quickly. In Series V neither seems to have started promptly, which gives to the reaction the appearance of acceleration. Sometimes it is difficult to induce substances to dissolve as quickly as it is desirable for such work even though more than enough of the solvent is present. Series VI gave a good constant for the meta. The para could not be trusted to dissolve readily enough at this temperature. The few determinations here made with benzamide do not warrant any conclusions.

Series VIII and IX with caustic potash, which was likewise prepared from potassium sulphate and barium hydrate, practically duplicate the corresponding ones with caustic soda. In Series VIII it was known that the meta did not dissolve quickly, which accounts for the low value of the constant at first.

Series X and XI with barium hydrate gave much higher constants than those with either caustic soda or potash. This is attributable to the absence of the neutral salt. The salt which was formed during the reaction retards it very markedly. The great influence of the neutral salts was not realized until these experiments were made, otherwise the excess

[1] J. prakt. Chem. (2) **35**, 112.

of sodium and potassium sulphate in the previous series would have been avoided.

Influence of Temperature.—The presence of sodium sulphate in the experiments with caustic soda deprive the results of much of their value, but as about the same amount was present in each case some conclusions may be drawn as to the relative velocities at different temperatures. For *m*-nitrobenzamide the average constants found were :

60°.	70°.	80°.	90°.	100°.
0.058	0.107	0.184	0.305	0.485

The values were plotted and the constants for intermediate degrees estimated from the curve. When this series of values was examined its members were found to be very nearly the geometrical progression. A geometrical series was calculated, assuming 0.058 and 0.485 as extremes. The two are here given.

60°.	70°.	80°.	90°.	100°.	
0.058	0.107	0.184	0.305	0.485	Experiment
0.058	0.099	0.168	0.285	0.485	Calculated

The agreement is as close as could be expected considering the known errors of the constants. Such a law as this would make it easy to compare results obtained at temperatures not too far apart, such, for instance, as the temperature of boiling water under various atmospheric pressures. It is intended to make and use such a temperature curve for reducing to "standard conditions" the results of the various experiments of Group III.

Van 't Hoff and others have shown that the variation of the constant for temperature should be of the form

$$\frac{dl.\ k}{dT} = \frac{A}{T^2} + B,$$

in which T is absolute temperature and A and B are quantities depending on the nature of the reaction.

Berthelot has shown in esterification experiments that in this expression A may be o when it takes the form $K = ab^t$, which agrees exactly with the conclusion reached above.

The few experiments made with *o*-nitrobenzamide show

that it resists hydrolysis by caustic soda about as well as it resists the influence of the acid.

Experiments, Group III.—The experiments with the various amides studied were made under as nearly the same conditions as convenient, so that the results should be more directly comparable. The earlier results are, of course, not quite so good as those obtained later. It is regretted that in so many instances numbers occur which are out of harmony with their environment. These are due to various causes, sometimes to mistakes in measuring the samples, or in reading burettes, and sometimes to causes unknown. In making up the average results the liberty was taken of throwing out figures evidently erratic.

p-Amidobenzamide has so far failed to give satisfactory results. It was hard to get the distillate to come over neutral, and there seems to be something in it which interferes with the end-reaction in titrating. *p*-Chlor- and *p*-brombenzamides went into solution slowly and as the corresponding acids were formed they crystallized out even at 100° C., and seemed to bring down some of the amides with them. This led to several series in which half quantities were used. Those gave much higher and, in general, better results, but here analytical difficulties were much increased, as complete decomposition gave only 20 mg. ammonia in many cases. Even 1 per cent of this amount is rather a small amount of ammonia. The results obtained in a similar series with *p*-nitrobenzamide were about 4 per cent higher than those at the ordinary concentration even after allowing for the unusually high barometer. The cause of this is not yet known.

The possibilities of the method may be judged from the experiments with *m*-nitrobenzamide in Series VI, according to the new method, in which the total variation is only 2 per cent of the value of the constant. This variation in the constant may be accounted for by an error of several tenths of a per cent in the analyses.

CONCLUSIONS.

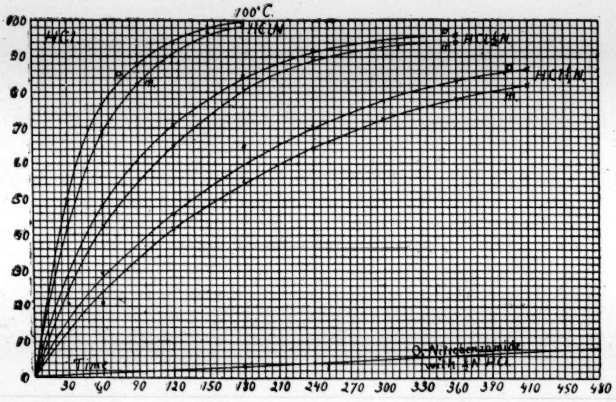
The results obtained with the meta- and para-substituted benzamides go to show that groups in these positions usually exercise some, though not a very marked retarding influence

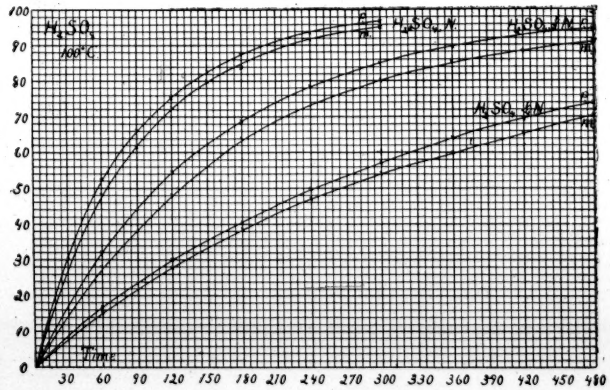
on the rate of hydrolysis. The rate does not seem to vary inversely as the molecular weight as Kellas concludes from his experiments on the etherification of meta-substituted benzoic acids. The nitro-group in the para position causes a very marked increase in the speed of hydrolysis.

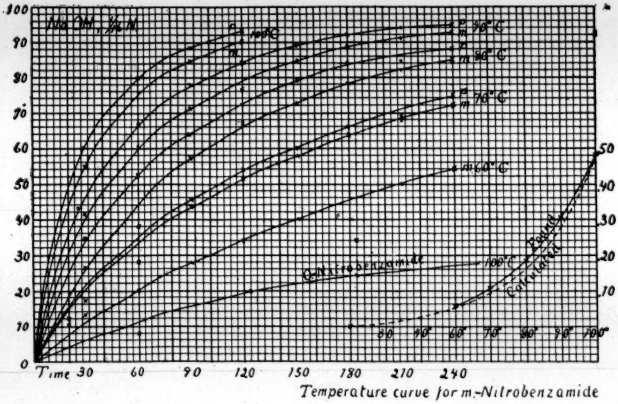
The experiments with ortho-substituted benzamides all show that groups in this position exert a remarkable "protective" influence on the amide group. With similar groups this influence varies roughly with the weight of the group but otherwise it seems to depend more upon the nature than the weight of the group. For instance, methyl with a weight of 15 protects far better than chlorine, or even than the methoxy group —OCH_3. The nitro-group is remarkable in its protective power, for though it has a weight of only 46 it "protects" more than twice as much as iodine (126). The methoxy and ethoxy groups are remarkable on account of their slight influence—far less than that of hydroxyl.

The general results reached by V. Meyer, Sudborough, Kellas, and others on the rate of formation of ethereal salts are generally in harmony with those here found, except that in the formation of ethereal salts the weight of the group seems to be of far more importance than its nature. Kellas found the nitro-group in the ortho position to have an exceptional retarding influence. The two lines of investigation seem entirely analogous and, when they have been more thoroughly worked out, it will be interesting to compare the results. The study of the hydrolysis of amides seems to have many advantages over the other. The experiments are so much simpler, and the reactions are better understood and are generally freer from complications. The reaction does not take place at such low temperatures as does the formation of ethereal salts. The possibility of using water solutions is no small advantage. The greatest advantage is a simple and direct method of analysis. Many of the results recorded in this article are brought together graphically in curves.

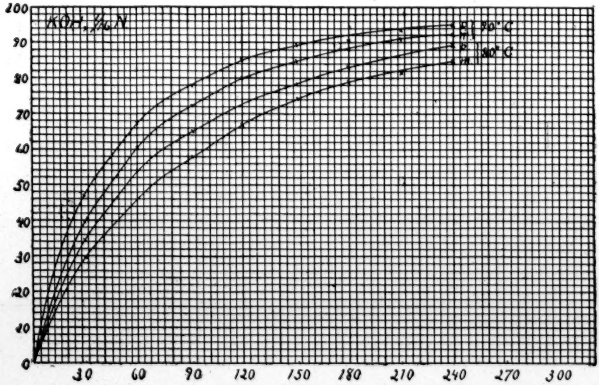
In a subsequent article some further results with these amides and with several others will be given, as well as the results of the study of the hydrolysis of these amides with alkali.

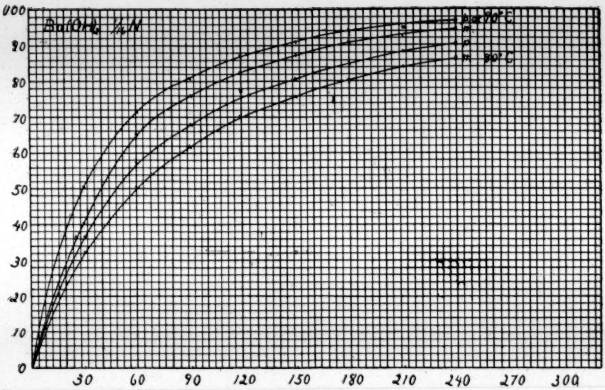

100°C.
HCl
HCl N
½ HCl N
¼ HCl N
Time
30 60 90 120 150 180 210 240 270 300 330 360 390 410 450 480

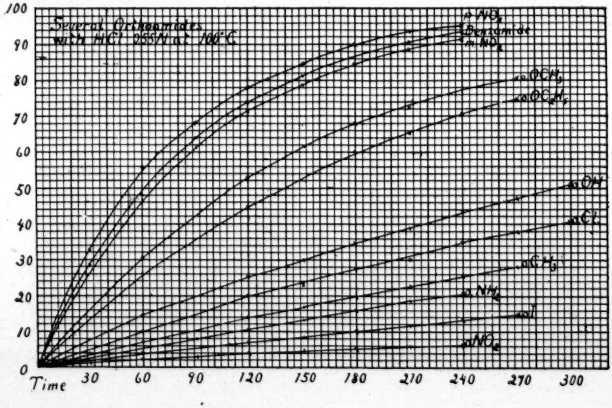

H_2SO_4
100°C.
H_2SO_4 N
H_2SO_4 ½N
H_2SO_4 ¼N
Time
30 60 90 120 150 180 210 240 270 300 330 360 390 420 450 480



Temperature curve for m.-Nitrobenzamide







CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
February, 1899.

ALIPHATIC SULPHONIC ACIDS.

III.—(1)-Bromethylenesulphonic Acid.

By Elmer P. Kohler.

Bromine reacts with ethylenesulphonic acid to form a monobrom substitution-product. In a previous paper[1] I showed that this is probably (1)-bromethylenesulphonic acid, $CH_2=CBrSO_3H$. This formula has since been definitely established by transforming the substance into bromsulphoacetic acid, $CHBr\begin{matrix}COOH\\SO_3H\end{matrix}$. This acid can only be formed from one in which the bromine atom and the sulphonic acid group are in combination with the same carbon atom.

This paper contains an account of the results obtained by a study of (1)-bromethylenesulphonic acid, and of those acids which are formed from it by direct addition of other substances. The material is presented under the following heads:

I. (1)-Bromethylenesulphonic acid.

II. (1,2)-Bromoxyethanesulphonic acid.

III. (1,2)-Dibromethanesulphonic acid.

IV. Acids formed by the action of sulphuric acid on bromethylenesulphonic acid.

I. (1)-BROMETHYLENESULPHONIC ACID.

Preparation.—An aqueous solution of the acid is obtained by liberating it from the lead salt,[2] filtering, and removing the excess of hydrogen sulphide by boiling. In dilute aqueous solution the acid is quite stable; after boiling a solution containing approximately 6 grams of acid in 100 cc. of solution, for five hours, it gave only a faint reaction for hydrobromic acid and no reaction for sulphuric acid. On neutralizing with potassium carbonate, evaporating to dryness, and extracting with 95 per cent alcohol only 0.4 gram of material insoluble in alcohol was obtained. This was the potassium salt of (1,2)-bromoxyethanesulphonic acid described below.

[1] This Journal, **20**, 694. [2] *Ibid.*, **20**, 693.

The alcoholic solution was evaporated to dryness and the residue analyzed. It contained 17.1 per cent potassium instead of 17.33 per cent calculated for $C_2H_4BrSO_4K$. On boiling the aqueous solution, therefore, there is no change except an exceedingly slow addition of water. If, however, the aqueous solution is evaporated on the water-bath or in a vacuum, over phosphorus pentoxide, a point is reached beyond which it is impossible to concentrate it without decomposing the acid. The liquid becomes dark in color, hydrobromic acid and sulphur dioxide are split off, and there is left a pasty mass from which no pure substances were obtained. As ether does not extract the acid from its solution in water, the pure acid could not be isolated.

Salts.—The salts were prepared by neutralizing cold solutions of the acid with carbonates or oxides. All the salts are extremely soluble in water, most of them are hygroscopic, and only the salts with the alkali metals crystallize well. Only the potassium, sodium, and barium salts were analyzed.

The potassium salt was described in an earlier paper, where a complete analysis is given.

The sodium salt, crystallized from absolute alcohol, washed with ether, and dried at 50°, gave the following results on analysis:

I. 0.1510 gram salt gave 0.0522 gram Na_2SO_4.

II. 0.1488 gram salt gave 0.0512 gram Na_2SO_4.

	Calculated for $C_2H_4BrSO_3Na$.	Found. I.	II.
Na	11	11.2	11.15

The salt is deliquescent and cannot be crystallized from water. It is readily soluble in ordinary alcohol, difficultly soluble in absolute alcohol, insoluble in ether. From alcohol it crystallizes in long, flat needles.

The barium salt crystallizes from water in long hydrous needles, which lose water and crumble as soon as they are removed from the mother-liquors. From the concentrated aqueous solution absolute alcohol precipitates an anhydrous salt in small needles.

I. 0.1794 gram salt gave 0.0820 gram $BaSO_4$.

II. 0.2012 gram salt gave 0.0926 gram $BaSO_4$.

	Calculated for $C_2H_3BrSO_3Ba$.	Found. I.	II.
Ba	27.02	26.9	27.1

The salt is readily soluble in water, insoluble in absolute alcohol.

(1)-*Bromethylenesulphone Chloride.*

The dry potassium salt reacts with phosphorus pentachloride in the cold. Under these conditions, however, very little sulphone chloride is obtained, as the reaction goes too far, the sulphonic acid group being replaced by chlorine. A better yield of chloride was obtained by adding the pentachloride to the finely powdered potassium salt suspended in chloroform, and boiling until all the salt was transformed. The chloroform and chlorides of phosphorus were removed by distillation under diminished pressure, the residue repeatedly washed with ice-water, and dried in a vacuum over phosphorus pentoxide.

I. 0.2820 gram chloride gave 0.1977 gram AgCl.

II. 0.2212 gram chloride gave 0.1551 gram AgCl.

	Calculated for $C_2H_3BrClSO_2$.	Found. I.	II.
Cl	17.11	17.4	17.4

The chloride is an oily liquid which cannot be distilled without decomposition, even in a vacuum. It does not solidify at —20°. When boiled with water it passes back into the acid, not a trace of sulphur dioxide or hydrobromic acid being split off.

Oxidation of (1)-*Bromethylenesulphonic Acid.*

The acid behaves towards oxidizing agents like ethylenesulphonic acid. Potassium permanganate, silver oxide, nitric acid, and barium manganate were tried. The products in all cases were carbon dioxide, sulphuric acid, hydrobromic acid, and water.

Reduction.

The acid is easily reduced. Even on boiling the neutral solution of the potassium salt with zinc or magnesium powder the bromine is slowly replaced by hydrogen. In the presence of free acid the reduction is much more rapid. In either case,

however, it stops with the formation of ethylenesulphonic acid and is quantitative.

An excess of zinc powder was added to 10 grams of the potassium salt, dissolved in 100 cc. of water, the solution heated to boiling, and hydrochloric acid added, drop by drop, until all the zinc was dissolved. The liquid gave no reaction for sulphide, sulphite, or sulphate, showing that the sulphonic acid group had been left intact. The zinc was removed with ammonium sulphide, the ammonium chloride and bromide with lead oxide, the liquid evaporated to dryness, and the residue extracted with alcohol. It gave 6.1 grams of pure potassium ethylenesulphonate instead of 6.5 grams calculated according to the equation:

$$\begin{matrix} CH_2 \\ \| \\ CBrSO_3K \end{matrix} + H_2 = \begin{matrix} CH_2 \\ \| \\ CHSO_3K \end{matrix} + HBr.$$

Replacement of Bromine by Double Decomposition.

The ease with which hydrogen is substituted for the bromine suggested the possibility of replacing it by double decomposition. Many experiments were made in this direction, but, with one exception, all were unsuccessful. The acid reacts only with substances which, like potassium cyanide, have an alkaline reaction. These invariably split off the sulphonic acid group along with the bromine. The one exception is the reaction with mercuric chloride. When an alkaline solution of the potassium salt is boiled with a large excess of mercuric chloride the bromine is slowly replaced with chlorine. After removing the mercury and halogen in the usual way a potassium salt is obtained which crystallizes from alcohol in small plates.

I. 0.1814 gram salt gave 0.0876 gram K_2SO_4.

II. 0.2265 gram salt gave 0.1087 gram K_2SO_4.

	Calculated for $C_2H_3ClSO_3K$.	Found. I.	II.
K	21.61	21.6	21.5

Behavior towards Halogens.

As an unsaturated acid, bromethylenesulphonic acid is capable of combining with other substances. It is not possi-

ble, however, to add the halogens or hypochlorous acid. In aqueous solution the acid and its salts slowly react with bromine, but the result is oxidation. Carbon dioxide is given off and sulphuric acid is found in the solution. Two grams of the potassium salt reacted with 7.4 grams of bromine. The equation,

$$C_2H_4BrSO_3K + 10Br + 5H_2O = 2CO_2 + 11HBr + KHSO_4,$$

requires 7.1 grams of bromine for 2 grams of salt. On evaporating to dryness, the residue was found free from organic matter. In aqueous solution, therefore, bromine oxidizes the acid to carbon dioxide and water.

Chlorine and hypochlorous acid react in the same way, oxidizing the substance rapidly at 0°. Iodine has no action.

To avoid the presence of water a solution of the acid in acetic acid was prepared as follows: An aqueous solution of the acid was concentrated, as far as possible, in a vacuum. The amount of sulphonic acid present per gram of this solution was determined by neutralizing with standard base. The solution was then mixed with glacial acetic acid and the quantity of acetic anhydride, calculated to combine with all the water present, added. This solution does not react with bromine below 80°. At this temperature the bromine attacks both the unsaturated acid and the solvent. The result is a mixture which was not separated. It was found, however, that the reaction with the unsaturated acid was addition, as the solution contains no sulphuric acid, and the amount of hydrobromic acid formed is only a small fraction of the amount calculated for substitution.

Addition of Water.

(1)-Bromethylenesulphonic acid combines with water more readily even than ethylenesulphonic acid. On simply boiling aqueous solutions of the acid or its salts there is a slow combination with water. At 120° a ten per cent solution of the acid passes quantitatively into bromethylenesulphonic acid in less than three hours. In the presence of a small quantity of an alkaline carbonate or an inorganic acid the addition takes place on the water-bath. If, for example, the solution ob-

tained by treating a solution of ethylenesulphonic acid with bromine, is concentrated on the water-bath and then neutralized, very little salt of the unsaturated acid is obtained,—in the presence of the hydrobromic acid the unsaturated acid passes into the oxy-acid while the solution is being concentrated. Alcohol and many soluble salts similarly favor the addition. In fact, in nearly all the experiments with the acid, some is lost in this way.

II. (1,2)-BROMOXYETHANESULPHONIC ACID.

It will be shown below that the acid formed by the addition of water to (1)-bromethylenesulphonic acid is (1,2)-bromoxyethanesulphonic acid.

$$\begin{matrix} CH_2 \\ \| \\ CBrSO_3H \end{matrix} \quad + \quad \begin{matrix} OH \\ | \\ H \end{matrix} \quad = \quad \begin{matrix} CH_2OH \\ | \\ CHBrSO_3H \end{matrix}.$$

The acid itself could not be obtained in crystalline condition, hence it was not analyzed. The salts were obtained by adding water to the salts of bromethylenesulphonic acid. They are easily separated from the latter as they are insoluble in alcohol and crystallize well from water.

Salts.—The sodium salt crystallizes from water in very characteristic conical aggregates.

I. 0.2455 gram salt lost 0.0095 gram H_2O at 130°.

II. 0.3135 gram salt lost 0.0115 gram H_2O at 130°.

III. 0.4224 gram anhydrous salt gave 0.1630 gram CO_2, and 0.0722 gram H_2O.

IV. 0.2360 gram anhydrous salt gave 0.0730 gram Na_2SO_4.

V. 0.3026 gram anhydrous salt gave 0.094g gram Na_2SO_4.

	Calculated for $C_2H_4BrSO_4Na.\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	3.8	3.8	3.8

	Calculated for $C_2H_4BrSO_4Na$.	Found III.	IV.	V.
C	10.6	10.4	....	....
H	1.8	1.9	....	....
Na	10.1	...	10.2	10.1

The potassium salt crystallizes from water in small lustrous prisms. The air-dried salt contains 0.5 molecule of water, which it loses below 150°.

I. 0.3269 gram salt lost 0.0125 gram H_2O.
II. 0.2666 gram salt lost 0.0103 gram H_2O.

	Calculated for $C_2H_4BrSO_4K.\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	3.6	3.8	3.8

I. 0.3150 gram anhydrous salt gave 0.1147 gram K_2SO_4.
II. 0.2564 gram anhydrous salt gave 0.0103 gram K_2SO_4.

	Calculated for $C_2H_4BrSO_4K$.	Found. I.	II.
K	16.05	16.3	16.15

When the anhydrous potassium salt is heated in an oil-bath it melts at about 200° and begins to lose water a few degrees above this point. If the temperature is kept constant at 225° until the weight is constant, the loss is 4.2 per cent, which is somewhat more than 1 molecule of water for 2 molecules of salt. The amber-colored residue contains traces of bromide and sulphite. It does not react with bromine, and therefore contains no unsaturated acid. From the aqueous solution alcohol precipitates the potassium salt of dibromdiisethionic acid in thin flakes.

I. 0.2022 gram salt gave 0.0758 gram K_2SO_4.
II. 0.2212 gram salt gave 0.0834 gram K_2SO_4.

	Calculated for $C_4H_6Br_2S_2O_7K_2$.	Found. I.	II.
K	16.66	16.8	16.9

The salts of bromoxyethanesulphonic acid therefore behave like isethionates when heated:

$$2\ \begin{matrix}CH_2OH\\ |\\ CHBrSO_3K\end{matrix} = \begin{matrix}CH_2—O—CH_2\\ |\quad\quad |\\ CHBrSO_3K\ CHBrSO_3K\end{matrix} + H_2O.$$

I found it possible to pass from isethionic acid to the unsaturated ethylenesulphonic acid by first replacing the hydroxyl with acetyl, and then splitting off acetic acid by heating.[1]

$$\begin{matrix}CH_2OH\\ |\\ CH_2SO_3K\end{matrix} \rightarrow \begin{matrix}CH_2OCOCH_3\\ |\\ CH_2SO_3K\end{matrix} = \begin{matrix}CH_2\\ \|\\ CHSO_3K\end{matrix} + CH_3COOH.$$

The same reaction was tried with bromoxyethanesulphonic acid. The potassium salt was heated in an oil-bath with an

[1] This JOURNAL, **20**, 683.

excess of acetic anhydride until a clear liquid was obtained. The excess of the anhydride was removed with absolute alcohol and the residue recrystallized from ordinary alcohol. The potassium salt of (1,2)-bromacetoxyethanesulphonic acid was thus obtained in small lustrous needles, readily soluble in water, difficultly soluble in boiling alcohol.

0.3337 gram salt gave 0.1065 gram K_2SO_4.

	Calculated for $C_4H_6BrSO_5K$.	Found.
K	14.08	14.3

When this salt was heated in an oil-bath it remained unchanged until the temperature was nearly 300°. At this point acetic acid or acetic anhydride is given off, but the salt begins to turn black and no unsaturated acid can be isolated from the residue.

Reaction with Phosphorus Pentachloride.

The dry potassium salt of bromoxyethanesulphonic acid reacts so readily with phosphorus pentachloride that unless the mass is well cooled with ice-water the liquid becomes black. On pouring the product into ice-water a thick liquid is obtained which cannot be freed from phosphorus by washing and which contains only a small amount of chlorine. It slowly goes into solution in cold water. This solution contains (1,2)-bromoxyethanesulphonic acid as the only organic product. The substance is probably a sulpholactone formed according to the equation :

$$\begin{matrix} CH_2OH \\ | \\ CHBrSO_3K \end{matrix} + PCl_5 = \begin{matrix} CH_2{-}O \\ | \quad | \\ CHBr\ SO_2 \end{matrix} + POCl_3 + HCl + KCl.$$

This reacts with water to form the oxy-acid :

$$\begin{matrix} CH_2{-}O \\ | \quad | \\ CHBr\ SO_2 \end{matrix} + H_2O = \begin{matrix} CH_2OH \\ | \\ CHBrSO_3H \end{matrix}.$$

A corresponding nitrogen compound has been obtained from (2)-chlorethanesulphone chloride[1] and from (1,2)-ethanedisulphone chloride.[2]

[1] J. prakt. Chem. [2], **20**, 383. [2] This JOURNAL, **19**, 746.

(1) $\begin{matrix}CH_2Cl\\|\\CH_2SO_2Cl\end{matrix} + NH_3 = \begin{matrix}CH_2—NH\\|\quad\quad|\\CH_2\quad SO_2\end{matrix} + 2HCl.$

(2) $\begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + NH_3 = \begin{matrix}CH_2—NH\\|\quad\quad|\\CH_2—SO_2\end{matrix}.$

I have obtained similar lactones with the higher members of the oxysulphonic acids, and in a later paper I expect to show that the sulpholactone ring closes quite as readily in the β- as in the γ-position.

If the same potassium salt is suspended in chloroform and then treated with phosphorus pentachloride, the reaction takes place slowly and the product is colorless. After distilling off the chloroform and chlorides of phosphorus under diminished pressure and washing with ice-water, an oily liquid is obtained which, when dried in a vacuum over phosphorus pentoxide, has approximately the composition of chlorbromethanesulphone chloride.

I. 0.1850 gram substance, decomposed with water, gave 0.1118 gram AgCl.

II. 0.2125 gram substance gave 0.1325 gram AgCl.

	Calculated for $C_2H_2ClBrSO_2Cl$.	Found. I.	II.
Cl	14.62	15.0	15.1

The high percentage of chlorine is due to a small quantity of phosphorus oxychloride, which could not be removed without series loss of substance.

This chloride was decomposed with water and the product isolated in the form of the sodium salt, by the method previously described with other chlorides. The sodium salt, crystallized from alcohol and dried at 100° gave the following analytical results:

I. 0.4251 gram salt gave 0.1496 gram CO_2, and 0.535 gram H_2O.

II. 0.5211 gram salt gave 0.1815 gram CO_2, and 0.0657 gram H_2O.

III. 0.1621 gram substance gave 0.2176 gram AgCl,AgBr.

IV. 0.1323 gram substance gave 0.1820 gram AgCl,AgBr.

V. 0.5127 gram salt gave 0.1425 gram Na_2SO_4.

VI. 0.3049 gram salt gave 0.0875 gram Na_2SO_4.

	Calculated for $C_2H_3O_3SClBrNa$.	Found. I.	II.	III.	IV.	V.	VI.
C	9.77	9.6	9.5	...	...	..	..
H	1.22	1.4	1.5	...	...	..	..
Cl.Br	47.04	..	..	46.9	47.3	..	..
Na	9.36	..	..	...	...	9.2	9.2

When a dibromcarbonic acid, in which the two bromine atoms are in combination with adjoining carbon atoms, is reduced with zinc and acid, the two halogen atoms are eliminated, and an unsaturated acid is formed. It was of interest, therefore, to determine whether an analogous dihalogensulphonic acid would behave in the same way, as this would give a method for determining the structure of halogensulphonic acids and a new way of passing from an oxy to an unsaturated acid.

Twenty grams of the sodium salt described above were dissolved in water and boiled with zinc powder until no more zinc went into solution. The reduction took about five hours. The zinc and halogen were removed in the usual way, the solution evaporated to dryness, and the residue recrystallized from alcohol. 9.5 grams of sodium salt were obtained instead of 10.6 grams calculated according to the equation :

$$\begin{array}{l} CH_2Cl \\ | \\ CHBr \\ | \\ SO_3Na \end{array} + Zn = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ SO_3Na \end{array} + ZnClBr.$$

A sodium determination gave 17.8 per cent sodium instead of 17.6 per cent calculated for $C_2H_3SO_3Na$. The behavior towards permanganate and bromine was the same as that of ethylenesulphonic acid salts prepared in other ways. The behavior of these dihalogensulphonic acids towards zinc is therefore exactly the same as that of the corresponding carbonic acids.

Reduction of (1,2) Bromoxyethanesulphonic Acid.

It is much more difficult to reduce this acid than the one from which it is obtained by addition of water. An aqueous solution of the sodium salt was boiled with zinc powder for hours without getting a trace of zinc bromide into solution.

On adding dilute sulphuric acid and continuing to boil the bromine was slowly replaced, but the amount of zinc required was so large that it was difficult to isolate the reduction-product. With 2 per cent sodium amalgam and dilute sulphuric acid, however, the reduction was satisfactory. After removing the mercury most of the sodium sulphate was precipitated with alcohol, the filtrate from this evaporated to dryness, and the residue extracted with 90 per cent alcohol. From the alcoholic solution, on cooling, the sodium salt of oxyethanesulphonic acid separated in plates.

I. 0.1188 gram salt gave 0.0561 gram Na_2SO_4.

II. 0.1660 gram salt gave 0.0782 gram Na_2SO_4.

	Calculated for $C_2H_5SO_4Na$.	Found. I.	II.
Na	15.54	15.3	15.2

With phosphorus pentachloride this salt gave a chloride boiling at 200°, the boiling-point of (2)-chlorethanesulphone chloride. The salt is, therefore, sodium isethionate. This proves that in bromoxyethanesulphonic acid the hydroxyl and sulphoxyl groups are in the (1,2)-relation.

Oxidation.

Potassium permanganate oxidizes bromoxyethanesulphonic acid to carbon dioxide, water, hydrobromic acid, and sulphuric acid.

Ten grams of the potassium salt were warmed with the quantity of the normal permanganate solution required to oxidize the salt to bromsulphoacetic acid. When the color of permanganate had disappeared the liquid was neutral to litmus and gave reactions for carbonate, bromide, and sulphate. On concentrating it a considerable quantity of unoxidized salt crystallized out. No other organic compound was found. With weak acid permanganate the oxidation was slower but the products were the same.

Concentrated nitric acid oxidizes to oxalic acid.

The acid does not attack the substance in the cold. On warming the mixture on the water-bath all the sulphur is split off as sulphuric acid. On concentrating the strongly acid liquid on the water-bath and allowing to cool, oxalic acid

crystallizes out. Nitric acid leaves the carbon skeleton intact.

Silver oxide oxidizes to glycolic acid.

In hot aqueous solutions the acid rapidly reduces freshly precipitated silver oxide. Silver sulphate goes into solution while metallic silver, silver bromide, and an organic silver salt separate out. A quantity of this precipitate was digested with hydrochloric acid and the solution repeatedly extracted with ether. From the ethereal solution, on evaporation, a small quantity of a carbonic acid crystallized in thin plates melting at 78°. Analysis and properties showed that the substance is glycolic acid.

0.2820 gram substance gave 0.3247 gram CO_2, and 0.1345 gram H_2O.

	Calculated for $C_2H_4O_3$.	Found.
C	31.6	31.4
H	5.3	5.3

Barium manganate oxidizes to bromsulphoacetic acid.

It is evident that in all the above oxidations one of the changes is the replacement of bromine by hydroxyl thus forming an extremely unstable oxysulphonic acid. To avoid this it is necessary to have a perfectly neutral oxidizer, one that can be kept neutral during oxidation. Such a substance was finally found in barium manganate. If a current of carbon dioxide is passed into water in which barium manganate is suspended, barium carbonate is precipitated and the manganate passes into the permanganate. If an oxidizable substance is present, the permanganate is reduced as fast as formed, the barium being precipitated as carbonate while the manganese is precipitated in the form of hydrated oxides. The reaction therefore always remains neutral.

Ten grams of the potassium salt of bromoxyethanesulphonic acid were dissolved in 250 cc. of water, an excess of barium manganate added, and a current of carbon dioxide passed into the liquid until a permanent purple color of permanganate remained. The solution was then decolorized with a little alcohol, filtered, and the potassium removed with sulphuric acid and alcohol. The resulting liquid was heated to boil-

ing, neutralized with barium carbonate, and filtered. On cooling, a difficultly soluble barium salt crystallized out in colorless needles. An analysis of the air-dried salt gave the following results :

I. 0.2110 gram substance lost 0.0200 gram at 130°.

II. 0.2008 gram substance lost 0.0188 gram.

III. 0.2220 gram substance gave 0.1245 gram CO_2, and 0.0234 gram H_2O.

IV. 0.6552 gram substance gave 0.1585 gram CO_2, and 0.0236 gram H_2O.

V. 0.2245 gram substance gave 0.1200 gram AgBr.

VI. 0.2112 gram substance gave 0.1134 gram AgBr.

VII. 0.1820 gram substance gave 0.1197 gram $BaSO_4$.

VIII. 0.2001 gram substance gave 0.1395 gram $BaSO_4$.

	Calculated for $C_2HBrO_5SBa.2H_2O$.	Found. I.	Found. II.
H_2O	9.24	9.1	9.2

	Calculated for C_2HBrO_5SBa.	Found. III.	IV.	V.	VI.	VII.	VIII.
C	6.77	6.5	6.6	...	...	...	...
H	0.28	0.5	0.4	...	...	...	...
Br	22.6	..	..	22.8	22.9	...	...
Ba	38.7	..	..	...	...	38.7	38.5

The salt was easily reduced with 2 per cent sodium amalgam and sulphuric acid. The reduction-product was changed into the barium salt, which crystallized in the hard lustrous nodules characteristic of barium sulphoacetate.

The formation of bromsulphoacetic acid by the oxidation of bromoxyethanesulphonic acid proves the correctness of all the formulas used.

III. (1,2)-DIBROMETHANESULPHONIC ACID.

Bromethylenesulphonic acid and its salts readily combine with hydrobromic acid. 20-gram portions of the potassium salt were heated with fuming hydrobromic acid at 120° for five hours. On cooling, a considerable quantity of potassium bromide crystallized out. Enough water to dissolve this was added and the whole transferred to a flask and distilled under 20 mm. pressure until the organic potassium salt began to crystallize out. The rest of the hydrobromic acid was removed

with lead oxide and the liquid evaporated to crystallization. The pure potassium salt of dibromethanesulphonic acid crystallized out in compact, lustrous prisms moderately soluble in cold water, insoluble in alcohol.

I. 0.1716 gram substance gave 0.0497 gram K_2SO_4.

II. 0.3127 gram substance gave 0.0900 gram K_2SO_4.

III. 0.1524 gram substance gave 0.1899 gram AgBr.

IV. 0.1610 gram substance gave 0.1981 gram AgBr.

V. 0.4841 gram substance gave 0.1331 gram CO_2, and 0.0479 gram H_2O.

VI. 0.4211 gram substance gave 0.1189 gram CO_2, and 0.0378 gram H_2O.

	Calculated for $C_2H_2Br_2O_3SK$.	Found. I.	II.	III.	IV.	V.	VI.
C	7.84	...	...	...	...	7.5	7.7
H	0.98	...	...	...	...	1.1	1.0
Br	52.28	...	...	52.5	52.7	..	..
K	12.74	12.9	12.9	...	...	..	..

When a solution of this salt is boiled with zinc powder the two bromine atoms are eliminated and ethylenesulphonic acid is formed. The two bromine atoms must therefore be in combination with different carbon atoms and the addition of hydrobromic acid to bromethylenesulphonic acid must take place in the same way as that of water:

$$\begin{matrix} CH_2 \\ \| \\ CBrSO_3H \end{matrix} + \begin{matrix} Br \\ | \\ H \end{matrix} = \begin{matrix} CH_2Br \\ | \\ CHBrSO_3H \end{matrix}.$$

The formation of this salt under these conditions is interesting as this is the salt that would be expected to be formed in the reaction between ethylenesulphonic acid and bromine:

$$\begin{matrix} CH_2 \\ \| \\ CHSO_3K \end{matrix} + \begin{matrix} Br \\ | \\ Br \end{matrix} = \begin{matrix} CH_2Br \\ | \\ CHBrSO_3K \end{matrix},$$

instead of the monobromethylenesulphonic acid always obtained:

$$\begin{matrix} CH_2 \\ \| \\ CHSO_3K \end{matrix} + Br_2 = \begin{matrix} CH_2 \\ \| \\ CBrSO_3K \end{matrix} + HBr.$$

The salt is, moreover, remarkably stable in the presence of water. No hydrobromic acid is given off below the boiling-point of water. Solutions were repeatedly warmed on the water-bath for days without giving a trace of silver bromide with a solution of silver nitrate. On boiling the solution, hydrobromic acid is slowly formed, but the solution contains no unsaturated acid. The hydrobromic acid is due to a reaction with water, resulting in the formation of (1,2)-bromoxyethanesulphonic acid:

$$\begin{array}{l} CH_2Br \\ | \\ CHBrSO_3K \end{array} + HOH = \begin{array}{l} CH_2OH \\ | \\ CHBrSO_3K \end{array} + HBr.$$

In view of these results the experiments with ethylenesulphonic acid and bromine were repeated, fuming hydrobromic acid being used as a medium in place of water. The reaction takes place much more slowly than in water alone, but the product is the same. After removing the hydrobromic acid and evaporating to dryness, the residue was completely soluble in alcohol; hence, not more than a trace of addition-product can have been formed.

There is an interesting difference in the behavior of the salts of (1,2)-dibromethanesulphonic acid towards those substances which are commonly used for replacing halogen with hydroxyl. It was shown above that when the potassium salt is boiled with water only the bromine atom in the (2)-position is replaced. Potassium carbonate (in dilute solution), potassium acetate, and freshly precipitated silver oxide, react like water. The (2)-bromine atom can be completely replaced with hydroxyl by any of these substances without getting a trace of sulphite into solution. Potassium hydroxide and barium hydroxide attack only the (1)-bromine atom, probably forming a (1)-oxysulphonic acid, which is decomposed as fast as formed, as a molecule of sulphite is formed for every atom of bromine replaced. The difference is illustrated by the following equations:

(1) $$\begin{array}{l} CH_2Br \\ | \\ CHBrSO_3K \end{array} + AgOH = \begin{array}{l} CH_2OH \\ | \\ CHBrSO_3K \end{array} + AgBr.$$

(2) $\begin{matrix}CH_2Br\\|\\CHBrSO_3K\end{matrix} + KOH = \begin{matrix}CH_2Br\\|\\CHOHSO_3K\end{matrix} + KBr.$

(3) $\begin{matrix}CH_2Br\\|\\CHOHSO_3K\end{matrix} + KOH = \begin{matrix}CH_2Br\\|\\CHO\end{matrix} + K_2SO_4 + H_2O.$

IV. SULPHONIC ACIDS FORMED BY THE ACTION OF SULPHURIC ACID ON (1)-BROMETHYLENESULPHONIC ACID.

The salts of bromethylenesulphonic acid dissolve in an excess of sulphuric acid forming a number of different sulphonic acids depending upon the conditions.

If only a slight excess of sulphuric acid is used, and the temperature kept below 80°, the only product is monobromethionic acid. 20 grams of the barium salt were mixed with an equal weight of sulphuric acid and the temperature kept at 75° for an hour. The liquid was cooled, slowly poured into a liter of ice-water, and neutralized with barium carbonate, ice being added from time to time to keep the liquid at 0°. The neutral liquid was set aside for several days to allow the barium sulphate to settle. The clear solution was then drawn off and concentrated in a vacuum, when a barium salt crystallized out in large colorless plates, mixed with a small quantity of barium carbonate. The salt was redissolved in cold water and concentrated as before. An analysis of the salt, dried on blotting paper, gave the following result:

I. 0.1706 gram salt gave 0.0940 gram $BaSO_4$.

II. 0.2569 gram salt gave 0.1438 gram $BaSO_4$.

	Calculated for $C_2H_3O_4BrO_3Ba$.	Found. I.	II.
Ba	32.62	32.4	32.8

The salt is readily soluble in cold water. If this solution is boiled barium sulphate is precipitated and (1,2)-bromoxyethanesulphonic acid remains in solution. It is, therefore, the barium salt of bromethionic acid formed by addition of sulphuric acid:

$$\begin{matrix}CH_2\\\|\\CBrSO_3H\end{matrix} + \begin{matrix}OSO_3OH\\|\\H\end{matrix} = \begin{matrix}CH_2OSO_3OH\\|\\CHBrSO_3OH\end{matrix}.$$

If the barium salt of bromethylenesulphonic acid or the barium salt just described, is mixed with an excess of sul-

phuric acid and the temperature kept at 125° for a few hours an amber-colored liquid is obtained which contains a different sulphonic acid. On neutralizing this liquid as in the preceding experiment, a clear liquid was obtained which became acid on standing. This acidity was not due to sulphuric acid, because no barium sulphate was formed. After neutralizing two or three times in this way and finding the liquid acid after standing for some time, it was finally digested with barium carbonate at 50° until no more barium sulphate was precipitated, then set aside in a vacuum over phosphorus pentoxide. In a short time a very difficultly soluble barium salt separated out in shiny plates, which could not be redissolved without decomposition. An analysis of the hydrous, slightly colored salt gave the following result:

I. 0.6218 gram substance gave 0.0957 gram CO_2, and 0.0893 gram H_2O.

II. 0.5880 gram substance gave 0.0884 gram CO_2, and 0.0687 gram H_2O.

III. 0.2114 gram substance, oxidized with nitric acid, gave 0.2385 gram $BaSO_4$.

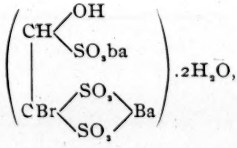
IV. 0.2281 gram substance, oxidized with nitric acid, gave 0.2561 gram $BaSO_4$.

V. 0.1620 gram substance, ignited with sulphuric acid, gave 0.0936 gram $BaSO_4$.

VI. 0.3104 gram substance, ignited with sulphuric acid, gave 0.1782 gram $BaSO_4$.

	Calculated for $C_3H_3O_{16}BrS_3Ba_{1.5}.2H_2O$.	Found. I.	II.	III.	IV.	V.	VI.
C	3.97	4.2	4.1	...	...	...	...
H	0.99	1.5	1.3	...	...	...	...
S	15.74	..	..	15.5	15.4	...	...
Ba	34.05	..	..	...	...	33.8	33.7

The salt was not quite pure but the results agree fairly well with the formula,



which is a bromine substitution-product of a substance obtained by Rathke[1] by the action of acid sulphites on chloral. This formula agrees well with the properties of the salt. When boiled with water, it is decomposed; barium sulphite is precipitated while the solution contains the barium salt of aldehydedisulphonic acid, which separates out on cooling. The salt is difficultly soluble, but can be recrystallized without change. It contains 2 molecules of water of crystallization which are not given off below 100°, where the substance begins to decompose.

I. 0.2613 gram substance gave 0.1332 gram $BaSO_4$.

II. 0.2526 gram substance gave 0.1270 gram $BaSO_4$.

	Calculated for $C_2HO_7BrS_2Ba.2H_2O$.	Found. I.	II.
Ba	30.17	30.0	29.8

The salt, like those of the unsubstituted acid described by Rathke,[2] is extremely sensitive to alkalies. When warmed with barium hydroxide the aldehyde group is split off as barium formate, which remains in solution while the more difficultly soluble barium salt of brommethanedisulphonic acid separates out from the hot solution in thin plates.

I. 0.2428 gram salt gave 0.1444 gram $BaSO_4$.

II. 0.2312 gram salt gave 0.1387 gram $BaSO_4$.

	Calculated for $CHBrS_2O_6Ba$.	Found. I.	II.
Ba	35.13	35.0	35.3

These results show that when sulphuric acid reacts with bromethionic acid two hydrogen atoms are replaced by sulphonic acid groups. The primary product seems to be an anhydride:

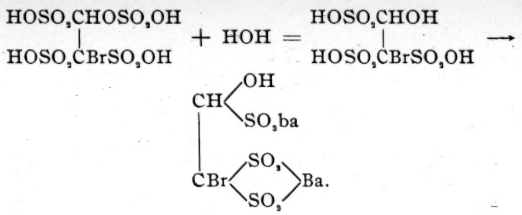
$$\begin{matrix} CH_2O.SO_2OH \\ | \\ CHBrSO_2OH \end{matrix} + 2H_2SO_4 = \begin{matrix} HOSO_2CH.O.SO_2 \\ | \\ HOSO_2CBrSO_2 \end{matrix} > O + 3H_2O.$$

This is slowly decomposed by cold water to form the acid:

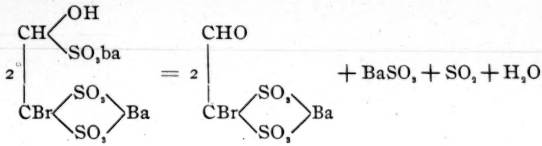
$$\begin{matrix} HOSO_2CH.O.SO_2 \\ | \\ HOSO_2CBrSO_2 \end{matrix} > O + H_2O = \begin{matrix} HOSO_2CH.O.SO_2OH \\ | \\ HOSO_2CBrSO_2OH \end{matrix}.$$

[1] Ann. Chem. (Liebig), **161**, 156. [2] *Ibid.*, **161**, 158.

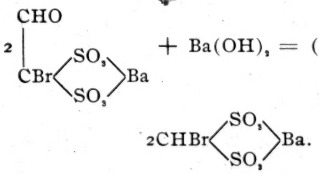
On warming with barium carbonate the sulphuric acid group is split off as sulphate, and the barium salt of bromoxyethanetrisulphonic acid remains :



Like all other (1,1)-oxysulphonic acid salts, this easily loses sulphite and passes into the aldehydesulphonic acid :



The aldehydesulphonic acids are easily decomposed by alkalies. On warming the last salt with barium hydroxide the aldehyde group is split off as formate and the barium salt of brommethanedisulphonic acid is left.



Summary.

When bromine reacts with ethylenesulphonic acid, dissolved in water, fuming hydrobromic acid, or glacial acetic acid, the first result is the substitution of bromine for the α-hydrogen atom. This shows a remarkable difference between saturated and unsaturated sulphonic acids. In satura-

ted sulphonic acids it is rarely possible to replace hydrogen with bromine; in the five unsaturated acids studied, substitution takes place at 0°.

The (1)-bromethylenesulphonic acid obtained in this way is extremely unstable. There is the same difference between the free acid and the salts, as was observed between polysulphone chlorides and the corresponding acids. When a moderately concentrated solution of the acid is heated to boiling and neutralized with a soluble carbonate from 35 to 50 per cent of it is decomposed—the bromine and sulphoxyl being split off as bromide and sulphite. If an equally strong solution of the potassium salt is boiled with the same carbonate there is rapid addition of water but no elimination of sulphite.

The bromine in bromethylenesulphonic acid behaves like bromine in other unsaturated compounds. Nascent hydrogen replaces it with hydrogen, potassium hydroxide with hydroxyl, and mercuric chloride with chlorine, but it does not lend itself to double decompositions, and it is impossible to link 2 molecules by eliminating halogen by silver.

(1)-Bromethylenesulphonic acid differs from the analogous carbonic acids, in that, like ethylenesulphonic acid, it shows no tendency to combine with two atoms of the same kind or with two similar groups. Thus, nascent hydrogen only replaces bromine with hydrogen; and bromine, chlorine, and hypochlorous acid oxidize in the cold. On the other hand, it combines with dissimilar atoms or groups far more readily than most unsaturated carbonic acids. Water, hydrobromic acid, sulphuric acid, acetic acid, and acid sulphites are all slowly taken up in the cold. In all of these cases the negative component of the molecule goes into the (2)-position. The result is a (1,2)-disubstituted ethanesulphonic acid. The (1,2)-oxyethanesulphonic acid obtained in this way is bromisethionic acid, $\begin{matrix} CH_2OH \\ | \\ CHBrSO_3H \end{matrix}$. A comparison between the two shows an important difference in the formation of anhydrides and in the behavior towards oxidizing agents. When isethionates are heated they lose a molecule of water for two molecules of salt and pass into diisethionates. The salts of

bromisethionic acid behave in the same way, but they are also capable of forming anhydrides from 1 molecule of salt:

$$\begin{array}{l} CH_2OH \\ | \\ CHBrSO_3K \end{array} + PCl_5 = \begin{array}{l} CH_2\!-\!O \\ | \quad | \\ CHBrSO_2 \end{array} + KCl + POCl_3 + HCl.$$

No such reaction is possible with isethionic acid. The product is always 2-chlorethanesulphone chlorides.

With potassium permanganate, isethionates always give sulphoacetates which are not affected by an excess of oxidizing agent. The same oxidizing agent completely destroys the bromisethionates even if the liquid is kept neutral with a current of carbon dioxide. The behavior of (1,2)-bromoxyethanesulphonic acid towards different oxidizing agents is interesting:

I. $\begin{array}{l} CH_2OH \\ | \\ CHBrSO_3H \end{array} + 5O(Br_2, Cl_2, HOCl, KMnO_4) = 2CO_2 + H_2O + HBr + H_2SO_4.$

II. $\begin{array}{l} CH_2OH \\ | \\ CHBrSO_3H \end{array} + 4O(HNO_3) = \begin{array}{l} COOH \\ | \\ COOH \end{array} + H_2SO_4 + HBr.$

III. $\begin{array}{l} CH_2OH \\ | \\ CHBrSO_3H \end{array} + 2O(Ag_2O + H_2O) = \begin{array}{l} CH_2OH \\ | \\ COOH \end{array} + H_2SO_4 + HBr.$

IV. $\begin{array}{l} CH_2OH \\ | \\ CHBrSO_3H \end{array} + 2O(BaMnO_4 + CO_2) = \begin{array}{l} COOH \\ | \\ CHBrSO_3H \end{array} + H_2O.$

Two (1,2)-dihalogen ethanesulphonic acids were obtained, one by the action of phosphorus pentachloride on bromoxyethanesulphonic acid; the other by direct addition of hydrobromic acid to bromethylenesulphonic acid. The salts of these acids are quite stable. By prolonged boiling with water, alkaline carbonates, acetates or silver oxide, the 2-halogen can be completely replaced with hydroxyl, while the (1)-halogen and the sulphonic acid group are left intact. The alkalies and barium hydroxide, on the other hand, instantly

attack the (1)-halogen in the cold, splitting off halogen and the sulphonic acid group, and leaving aldehydes or their polymeric products. With zinc or magnesium both of the halogens can be eliminated with the greatest ease, leaving an unsaturated acid.

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A SERVICEABLE GENERATOR FOR HYDROGEN SULPHIDE.

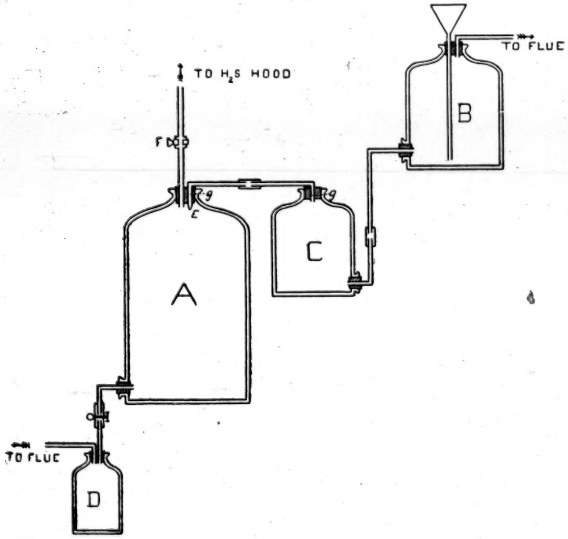
BY W. P. BRADLEY.

The number of gas generators which have been described in chemical periodicals and in part put upon the market is so great that one hesitates before inflicting another upon a long-suffering public. A generator for hydrogen sulphide, however, is subjected by the ordinary class of analytical students to demands so exacting, that probably very few will be found which have met those demands for a period of years with entire satisfaction.

The apparatus to be described has been in use in the laboratory of Wesleyan University in essentially its present form for nine years, and during the latter half of that time has given entire satisfaction both to students and to those who have had the care of it. It consists principally of three glass bottles, *A*, *B*, and *C*, each provided with an orifice near the bottom. *A* is the generator proper, whose mouth is wide so as to admit large lumps of iron sulphide, and whose height is about three times its diameter. It has a capacity of about 16 liters. Through the rubber stopper which closes its mouth passes the gas main, controlled by the main cock *F*, and terminating at a suitable hood in as many distributing cocks as may be desired. Students have access to the distributing cocks only. Through the same stopper enters the acid-supply tube, drawn down at the end *E* to a jet capable of delivering a stream of acid not thicker than the shank of an ordinary pin. This jet projects as little as possible below the stopper. Through the tubulure at the bottom, with its inner end just flush with the stopper, passes a rather thick-walled tube controlled below by a pinch-cock, as shown. By means of this tube the spent

acid is delivered either into a sink or waste-pipe capable of thorough flushing, or into a small bottle, *D*, connected with a flue, which may be detached just below the pinch-cock and emptied as required. The generator bottle is charged with large pieces of iron sulphide until completely full, and *should not be allowed to become less than half full* before recharging. The spent acid must never be allowed to accumulate in such quantities as to reach the top of the sulphide.

B is the acid reservoir, wide in proportion to its height,



with a capacity of about 8 liters. The stopper at its mouth admits a funnel whose neck is continued by a glass tube passing to the bottom of the bottle. This reservoir is connected with a flue as shown. The acid used is commercial hydrochloric, diluted with an equal volume of water. A proper charge of acid is the amount necessary to fill *B* half full when

acid is running from, or stands at, the jet *E*. The height at which the reservoir itself is fixed depends, of course, largely on the pressure to be overcome by the gas. A difference of level of 6 inches between the bottom of *B* and the top of *A* has been found ample for ordinary analytical work. If desired, an adjustable support may be used with this reservoir, so that the latter may be raised or lowered at will, and brought down to the level of *A* when the apparatus is not in use. In practice, however, it has been found much better to select once for all such an elevation as will yield somewhat more than the maximum pressure desired.

C is the gas reservoir, designed chiefly to retain whatever gas is made after the distributing-cocks, or *F*, are closed. Like *B* it is wide and low. It has a capacity of about 4 liters. Its mouth should be on exactly the same level as that of *A*, and the vertical portions of the tube connecting *C* and *A* are made as short as possible.

The tubing used in the apparatus is, of course, of glass. The rubber stoppers are protected with a thin coating of paraffin, crowded into place while the latter is still warm and soft, and firmly wired. The rubber connections are coated within with paraffin (by pouring hot paraffin through them when perfectly dry), and securely wired.

The working of the apparatus is evident from the foregoing description of its construction. The gas pressure in *A* depends on the difference in level between the top of the acid in *B* and the mouth of the jet *E*. When this pressure is relieved by drawing gas at *F*, a small quantity of acid flows in at the jet and trickles down through the iron sulphide. As soon as the action is fairly established, gas is produced somewhat in excess of the demand, and forcing back the acid, occupies the top of *C*. On the other hand, when the action slackens, the acid flows forward again, driving before it this accumulation. When the demand ceases entirely, gas continues to form slowly for a time, until the last portion of acid admitted is entirely spent. The gas so formed passes into the gas reservoir *C* and fills it from one-third to two-thirds full. Renewed demand for gas is met, of course, at first by this accumulated supply.

Among the special advantages attending the use of this generator may be mentioned economy of acid, uniform efficiency, perfect automatism, and consequently the very slight amount of attention required.

As between the two general types of generator—that in which the acid, after use, is forced back into the reservoir, and that in which the acid never returns, but remains in contact with the iron sulphide—the advantage in point of economy must always lie with the latter. In generators of the former type, either the acid must be discarded before it is completely spent, or else the apparatus begins to work so slowly as to be inefficient. Any one may easily test the matter by throwing a quantity of iron sulphide into a portion of so-called spent acid drawn from an ordinary Kipp apparatus or from any other generator of the former type. Action will take place, somewhat slowly of course, and a quantity of gas, greater or smaller, will be formed. Whatever this amount of gas may prove to be, it represents the loss involved in throwing away the acid in question. And this loss occurs inevitably, whether the spent acid is forced back, as in the Kipp, so as to stand between the fresh acid and the sulphide, or whether, by special arrangements, it is not allowed to return upon the sulphide until all of the acid fresher than itself has been given a chance to act. The amount of this loss may not be worth considering, perhaps, in the case of other gases than hydrogen sulphide, which on the whole are used in much smaller quantity, or even in the case of hydrogen sulphide itself when used for miscellaneous purposes, as in lecture experimentation, etc. But where gas is needed in quantities large in the aggregate, but varying greatly from one time to another, as is the case with hydrogen sulphide required for the work of classes in analysis, the loss from this source in the end is considerable. One who had never tested the matter would doubtless be surprised at the amount of acid thus thrown away. It is scarcely necessary to say that the apparatus now described shares the advantage of economy in this regard with generators of the second type, to which it belongs. Its acid, once admitted to reaction with the iron sulphide, never returns, but continues to act until entirely spent. At the same

time, the efficiency of the apparatus remains entirely constant, because maintained by a flow of uniformly fresh acid.

In being, within the limits of its capacity, entirely automatic, this generator is superior even to others of its own type. Quite universally, in these generators the flow of acid is regulated by a cock introduced somewhere between the reservoir and the generating chamber. This arrangement is sufficiently satisfactory where an unvarying flow of gas is desired or allowable, but requires that the apparatus be placed within easy reach of the operator. It is not advantageous where gas is wanted intermittently and in widely varying quantities, and for student work in analysis is entirely out of the question. With the arrangements here described, the student opens one of the distributing cocks when he wants gas, and turns it off again when he has finished. The flow of acid takes care of itself. The conditions in the hood are exactly the same as if the gas came directly from a gas-holder or storage tank.

To keep the generator in such condition as to meet the demands made upon it in this laboratory by a class of 25–30 students requires a very small amount of care and attention. On the morning of each working day the reservoir is charged with acid (accidents aside it is never found empty), the spent acid is drawn off, and the cock F leading into the main is opened, the entire amount of time required of the attendant not exceeding five minutes daily. The iron sulphide bottle is replenished twice a year only.

Finally, the apparatus is so simple that any one can construct it, and once put together it will not get out of order. In its construction tubulated bottles are not at all necessary. Any wide bottles of the proper relative size may be utilized by one who knows how to bore a hole in glass with a broken file.

For some kinds of work uniform gas pressure is required. This is a matter of minor importance in the case of analytical work for which the generator was designed. It is not claimed that this condition is perfectly met, but it can be confidently asserted that with wide, low bottles for B and C, and with B in position at a suitable height above the rest, as given, as uniform a flow of gas is obtained with this generator as with any now on the market, and more so than with most.

One grave objection might be raised to the use of a jet to regulate the flow of acid, namely, that it would be extremely likely to clog by the lodgment in it of solid matter, particularly of sulphur in the case of a generator for hydrogen sulphide. That this objection, which is almost always raised when the present apparatus has been described to those who have never seen it work, is practically of no weight, will appear in the statement that during the entire period of nine years over which the generator has been in use in this laboratory the jet has never clogged.

The dimensions of the various parts of the apparatus as given above are those which have been found on the whole to give the best results for our requirements. Some of them, however, may be varied within certain relative limits. The minimum size of *C* obviously depends on the size of the stream of acid admitted by the jet, for the larger this stream is the more irregular and jerky its flow will be, and the greater the quantity of residual gas to be stored when all the cocks are shut off. On the other hand, no good object could be served by selecting for *C* a bottle of such a volume as would more than accommodate the maximum amount of this residual gas. The acid reservoir *B* should, of course, be at least large enough to hold such a quantity of acid as is needed for the maximum run desired, plus all the acid which may be driven back into it from *C*. The dimensions given contemplate a total available acid charge of 4 liters, or half the volume of the reservoir. As it is highly desirable that the apparatus should not be in need of constant watching, the unoccupied interstitial space between the blocks of iron sulphide in *A* must at all times be as great as the volume of available acid remaining in *B*. If this is not the case, the spent acid may accumulate toward the end of a run so as to stand as high as the iron sulphide, after which, the acid which enters, being specifically lighter, will merely float on top, penetrating to the sulphide by gradual diffusion only, and generating almost no gas. The result of such a condition appears when next the spent acid is drawn off. No sooner does the top layer of unused acid come into contact with the iron sulphide than a quantity of gas is generated which is utterly uncontrollable. This obviously cannot

occur if the generator bottle can accommodate all the available acid of *B* without entirely submerging the iron sulphide. Herein lies the advantage of using the sulphide in as coarse a form as possible, and the reason for giving the generator bottle a capacity not less than twice that of the acid reservoir; *i. e.*, not less than four times the volume of the maximum available acid charge. With such precautions the column of iron sulphide may drop, by use, well down toward half its full height before it can become submerged, with the result that in this laboratory continuous use of the generator for half a year at a time is possible without replenishing the sulphide. Similar considerations indicate the desirability of drawing off the spent acid every time fresh acid is supplied to the reservoir.

It will be seen, therefore, that the actual dimensions stated in describing the apparatus represent a practical minimum with reference to the size of the jet used, and also that any reduction which is attempted in these must be attained by decreasing the size of the latter. How far this may be done without risk of clogging would have to be determined by actual experiment. Whether a small portable generator could be constructed on this principle is, in the judgment of the writer, doubtful. The one described above serves its purpose so well as to leave scarcely anything to be desired.

WESLEYAN UNIVERSITY,
Jan. 14, 1899.